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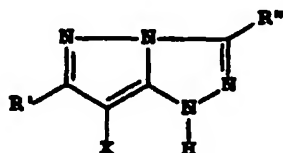
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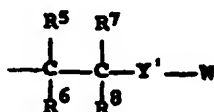
(54) **Processing of photographic elements using N,N-dialkylhydroxylamine antioxidants in photographic color developers**

(57) Certain N,N-dialkylhydroxylamine derivatives are useful as antioxidants in photographic color developer compositions. These compositions can be used to increase magenta dye density in color images provided by processing color photographic silver halide materials containing at least one magenta dye-forming color coupler having structure II:

form a ring, R<sup>8</sup> is hydrogen or a substituent, provided that R<sup>7</sup> and R<sup>8</sup> can together form a ring when R<sup>8</sup> is a substituent, Y' is -NH- or -CH<sub>2</sub>- and W is selected from the group consisting of -C(O)R<sup>9</sup>, -SO<sub>2</sub>R<sup>9</sup>, -P(O)(OR<sup>10</sup>)<sub>2</sub> wherein R<sup>9</sup> is any of an alkyl, aryl, alkoxy, aryloxy, alkylamino or arylamino group, and R<sup>10</sup> is an alkyl or aryl group.



wherein X is hydrogen or a coupling-off group, R' is a tertiary alkyl group, R'' is the group



wherein R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently hydrogen or alkyl groups, and any two of R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> can together

## Description

The present invention relates to methods for the processing of color photographic materials, and particularly to methods of color developing and photographic processing of photographic elements containing specific dye-forming couplers using color developing solutions containing specific antioxidants.

Photographic color developing compositions are used to process color photographic materials such as color photographic films and papers to provide the desired color images. Such compositions generally contain developing agents as reducing agents to react with suitable color forming couplers to form the desired dyes. However, such developing agents are susceptible to rapid oxidation by dissolved oxygen. As a result, such color developer compositions may remain active for only a short period of time, increasing the variability of the development process and requiring frequent replenishment.

In order to extend the activity of the color developing composition, an antioxidant is conventionally included to preserve the oxidation state of the color developer. Useful antioxidants must have certain properties including effective antioxidants effect, no effect on the color developer, low molecular weight and no objectionable odor.

Many classes of compounds have been employed as color developer solution antioxidants, including hydroxylamines, hydroxamic acids, oximes, nitroxy radicals, hydrazines, hydrazides, phenols, saccharides, various simple amines, polyamines, quaternary ammonium salts,  $\alpha$ -hydroxy ketones, alcohols, diamides and disulfonamides. To be used in practice, however, antioxidants must be soluble in aqueous media, non-toxic to living organisms, low cost and non-silver halide developers. Further, it is desirable that antioxidants react slowly with oxygen and rapidly with oxidized color developer, but not so rapidly that color development is retarded. Yet another concern is that the antioxidant must not be able to promote bacterial growth.

All of these considerations greatly limit the number and classes of compounds that practically can be used as antioxidants or stabilizers in color developer solutions. One class of compounds often used as antioxidants are substituted hydroxylamines. They exhibit excellent characteristics by having a slow rate of aerial oxidation, being non-silver halide developers, and are relatively inexpensive to produce. There are considerable references describing such compounds.

For example, US-A-4,892,804 describes a number of dialkylhydroxylamines useful as color developer antioxidants, including N,N-diethylhydroxylamine, which are improvements over the unsubstituted or mono-substituted hydroxylamines. US-A-4,876,174 describes a lengthy list of substituted hydroxylamines believed useful as antioxidants in color developer compositions, but the compounds actually used emit unpleasant odors. In US-A-5,354,646, water-solubilizing groups, such as carboxy and sulfo are shown on dialkylhydroxylamines.

EP 9609583.5, describes the use of certain N-(branched alkyl)-N-sulfoalkylhydroxylamines that are quite useful as antioxidants in photographic color developing solutions. Other useful antioxidants containing branched alkyl groups are known. These compounds were demonstrated to provide improved color developing solution stability over similar compounds having merely linear alkyl groups.

Photographic elements containing certain magenta 1H-pyrazolo[5,1-c]-1,2,4-triazole dye-forming couplers that provide excellent hue and image stability to light are known. However, when such elements are processed using conventional color developing solutions, it was observed that, in some instances, the maximum dye density was insufficiently high compared to what would be expected from the level of silver halide in the elements. It is desired to solve this problem.

The problems noted above are overcome by a method of processing comprising:

color developing an imagewise exposed color photographic silver halide material with a color developer composition comprising:

- (a) a color developing agent present in an amount of at least 0.001 mol/l, and
- (b) a hydroxylamine derivative characterized as having the formula I:



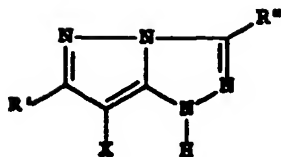
wherein R and R<sup>1</sup> are independently alkyl groups of 1 to 8 carbon atoms provided the total carbon atoms for R and R<sup>1</sup> is no greater than 9,

R<sup>2</sup> is an alkylene group of 2 to 6 carbon atoms, or a phenylene or benzylene group,

Y is sulfo, carboxy, hydroxy, phosphono, -SO<sub>2</sub>NR<sup>3</sup>R<sup>4</sup> or -CONR<sup>3</sup>R<sup>4</sup> wherein R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or a alkyl group of 1 to 3 carbon atoms,

the hydroxylamine derivative being present in the color developer composition in an amount of at least 0.001 mol/l,

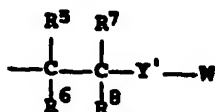
wherein the photographic material comprises at least one silver halide emulsion layer, the layer having in reactive association therewith, at least one magenta dye-forming coupler represented by the formula II:



wherein

X is hydrogen or a coupling-off group,

R' is a tertiary alkyl group, R\* represents the group



R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently hydrogen or alkyl groups, and any two of R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> can together form a ring,

R<sup>8</sup> is hydrogen or a substituent, provided that R<sup>7</sup> and R<sup>8</sup> can together form a ring when R<sup>8</sup> is a substituent, Y' is -NH- or -CH<sub>2</sub>-, and

W is -C(O)R<sup>9</sup>, -SO<sub>2</sub>R<sup>9</sup> or -P(O)(OR<sup>10</sup>)<sub>2</sub> wherein R<sup>9</sup> is any of an alkyl, aryl, alkoxy, aryloxy, alkylamino or arylamino group, and R<sup>10</sup> is an alkyl or aryl group.

Use of the hydroxylamine derivatives described herein in color developer compositions to process the noted photographic materials provides results that were heretofore unexpected. Specifically, it has been found that processing color photographic silver halide elements containing magenta dye-forming couplers described above with a color developing composition containing the noted hydroxylamine derivative provides an unexpected increase in magenta dye density (especially D<sub>max</sub> of the magenta dye). This gain in magenta dye density provides the option of more vivid colors in the resulting image, or the use of lowered amounts of coated silver halide. Both advantages provide obvious benefits that are desired in the photographic industry.

The hydroxylamine compounds useful in the practice of this invention that are useful as antioxidants can be represented by the formula I:



wherein R and R<sup>1</sup> are independently alkyl groups (linear or branched) of 1 to 8 carbon atoms (such as methyl, ethyl, *n*-propyl, isopropyl, isobutyl, *t*-butyl, *n*-butyl, pentyl, hexyl, 2-ethylhexyl and octyl groups). The total number of carbon atoms for both R and R<sup>1</sup> is no greater than 9 (that is, the branched alkyl group has 3 to 10 carbon atoms). Preferably, each of R and R<sup>1</sup> has 1 to 3 carbon atoms (so the branched alkyl group has from 3 to 7 carbon atoms), and more preferably, each is a methyl or ethyl group (so the branched alkyl group has 3 to 5 carbon atoms). Most preferably, each of R and R<sup>1</sup> is a methyl group (thus, the alkyl group is an isopropyl group). It is clear from the noted formula that one substituent of the nitrogen atom is a branched alkyl group wherein the carbon atom directly connected to the nitrogen has one and only one hydrogen atom.

Each of R and R<sup>1</sup> can be substituted with one or more substituents other than sulfo or carboxy groups, as long as such substituents do not adversely affect the antioxidant properties of the compound. Preferably, each of R and R<sup>1</sup> is an unsubstituted alkyl group (linear or branched).

In the noted formula, R<sup>2</sup> is a substituted or unsubstituted, branched or linear alkylene group of 2 to 6 carbon atoms (such as an ethylene, trimethylene, isopropylene, tetramethylene or hexamethylene group) and preferably, it has only 2 or 3 carbon atoms. Most preferably, R<sup>2</sup> is a substituted or unsubstituted ethylene group. The R<sup>2</sup> group can also be a substituted or unsubstituted phenylene or benzylene (that is, methylenephénylene) group. The substituents that can be attached to the R<sup>2</sup> groups include, but are not limited to, hydroxy, carbonamido, carboxy, sulfo, halo, sulfonamido or phosphono.

Preferably,  $R^2$  is an unsubstituted, linear alkylene group of 2 to 4 carbon atoms, unsubstituted phenylene or unsubstituted benzylene group. More preferably,  $R^2$  is an unsubstituted alkylene group of 2 or 3 carbon atoms, and most preferably, it is an unsubstituted ethylene group.

In the noted formula, Y is sulfo, carboxy, hydroxy, phosphono,  $-\text{SO}_2\text{NR}^3\text{R}^4$  or  $-\text{CONR}^3\text{R}^4$ . More preferably, it is sulfo, carboxy,  $-\text{SO}_2\text{NR}^3\text{R}^4$  or  $-\text{CONR}^3\text{R}^4$ , and most preferably, it is sulfo or carboxy. The noted acid forming groups can be present as free acids, salts or esters (having a suitable cation or ester group).

$R^3$  and  $R^4$  are independently hydrogen or a substituted or unsubstituted alkyl group of 1 to 3 carbon atoms. Preferably, each is hydrogen or the same alkyl group of 1 or 2 carbon atoms, and more preferably, each is hydrogen or a methyl group. In one embodiment, when Y is  $-\text{SO}_2\text{NR}^3\text{R}^4$ , each of  $R^3$  and  $R^4$  is an alkyl group of 1 to 3 carbon atoms as defined above.

Suitable monovalent cations or ester groups for the free acids include ammonium (including quaternary amines), alkali metal ion (such as sodium, potassium or lithium), an alkyl group having 1 to 4 carbon atoms (such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl and *t*-butyl), pyridinium, tetraethylammonium and tetramethylammonium, as well as other cations and ester groups which would be readily apparent to one skilled in the art. Preferably, methyl ester, ethyl ester or an alkali metal salt form is used.

Representative compounds useful in the practice of this invention include, but are not limited to, N-isopropyl-N-(2-ethylenesulfonic acid)hydroxylamine, N-sec-butyl-N-(2-ethylenesulfonic acid)hydroxylamine, N-isopropyl-N-(1-methylpropionic acid)hydroxylamine, N-isopropyl-N-(3-carboxypropyl)hydroxylamine, N-sec-butyl-N-(2-carboxyethyl)hydroxylamine, N-sec-butyl-N-(1-methyl-2-carboxyethyl)hydroxylamine, N-sec-butyl-N-(4-carboxybutyl)hydroxylamine, N-octyl-N-(3-carboxypropyl)hydroxylamine, N-isopropyl-N-(2-ethanephosphonic acid)hydroxylamine, N-isopropyl-N-(2-sulfonamidoethyl)hydroxylamine, N-isopropyl-N-(2-N-isopropylsulfonamidoethyl)hydroxylamine, N-isopropyl-N-( $\rho$ -carboxybenzyl)hydroxylamine, N-isopropyl-N-(2-carboxyethyl)hydroxylamine, bis(2-carboxyethyl)hydroxylamine, N-isopropyl-N-(2-N',N'-dimethylsulfonamidoethyl)-hydroxylamine, N-isopropyl-N-(2-N',N'-diethylsulfonamidoethyl)hydroxylamine, N-isopropyl-N-(2,2-dicarboxyethyl)hydroxylamine, N-sec-butyl-N-(2-carboxyethyl)hydroxylamine, N-isopropyl-N-(2-carbonamidoethyl)hydroxylamine, N-isopropyl-N-(2-N',N'-dimethylcarbonamidoethyl)hydroxylamine, N-isopropyl-N-(2-N'-isopropylcarbonamidoethyl)-hydroxylamine, and salts (for example, alkali metal) or esters (such as methyl or ethyl ester) of the free acids in this list.

Of the foregoing compounds, N-isopropyl-N-(2-ethylenesulfonic acid)hydroxylamine and N-isopropyl-N-(2-carboxyethyl)hydroxylamine are preferred, along with salts or esters of the free acids. The first compound is most preferred (along with obvious salts thereof).

The compounds described herein as useful antioxidants can be readily prepared using published procedures, such as those described in US-A-3,287,125, US-A-3,778,464, US-A-5,110,985, and US-A-5,646,327. Representative preparative methods are described below.

The antioxidant is included in the color developer composition in an amount of at least 0.001 mol/l. A preferred amount is at least 0.005 mol/l, and more preferably at least 0.01 mol/l. A preferred maximum amount is to 0.5 mol/l, and more preferably to 0.1 mol/l. These amounts are best in the practice of the invention to achieve the desired antioxidant effect and increase in  $D_{\text{max}}$  of the magenta dyes. More than one of the noted antioxidants can be used in the same color developer composition if desired, but preferably, only one is used.

In addition, the noted hydroxylamine antioxidant can be used in combination with one or more other secondary antioxidants, that is compounds known in the art as having antioxidant properties including, but not limited to, hydroxylamine (and salts thereof), hydrazines, amino acids, saccharides (including polysaccharides), alkanolamines, mono- and diamines and other compounds known in the art for this purpose. If present, the amounts of such compounds would be readily apparent to one skilled in the art, although when used in combination with the hydroxylamine derivatives noted above, less than conventional amounts of the secondary antioxidants may be acceptable.

In solution, the pH of the color developer composition is generally from 9 to 13 (preferably from 9 to 11), as provided by the addition of one or more weak or strong bases (such as a hydroxide) or buffers in amounts readily known in the art. Particularly useful buffers include, but are not limited to, carbonates, borates, tetraborates, phosphates, glycine salts, leucine salts, valine salts, proline salts, alanine salts, aminobutyric acid salts, lysine salts, guanine salts and hydroxybenzoates.

The color developer compositions include one or more color developing agents, of which there are hundreds of possibilities. Useful classes of such materials include, but are not limited to, aminophenols, *p*-phenylenediamines (especially N,N-dialkyl-*p*-phenylenediamines) and others that are well known in the art, such as EP-A 0 434 097 and EP-A 0 530 921. It may be useful for the color developing agents to have one or more water-solubilizing groups as are known in the art. Further details of such materials are provided in *Research Disclosure*, publication 38957, pages 592-639 (September, 1996). This reference will be referred to hereinafter as "*Research Disclosure*".

The one or more color developing agents are present in solution in conventional amounts, which are typically at least 0.001 mol/l and preferably from 0.005 to 0.05 mol/l.

A color developer composition can be easily prepared in the form of an aqueous solution by mixing a suitable color

developing agent (in a suitable solution) with an antioxidant as described above (in a suitable aqueous solution). Water can be added to the resulting solution to provide the desired concentrations of an aqueous solution, and the pH can be adjusted as noted above.

The composition can also include one or more of a variety of other addenda which are commonly used in such compositions, such as alkali metal halides (such as potassium chloride, potassium bromide, sodium bromide and sodium iodide), metal sequestering agents (such as polycarboxylic or aminopolycarboxylic acids or polyphosphonates), buffers (as noted above), other preservatives (such as sulfites), anti-foggants, development accelerators, optical brighteners, wetting agents, stain reducing agents, surfactants, defoaming agents, and water-soluble or water-dispersible color couplers, as would be readily understood by one skilled in the art (see for example, *Research Disclosure*, noted above and US-A-4,814,260). The amounts of such additives are well known in the art also. For example, the amounts of halides can be varied widely, but are preferably in the range of from  $5 \times 10^{-7}$  to 0.3 mol/l for chloride ion and from  $5 \times 10^{-7}$  to 0.1 mol/l for bromide ion. Iodide ion may be totally absent, or present up to an amount of 0.001 mol/l. A preferred color developer composition is described below in Example 1.

It is particularly useful for the color developer composition to include one or more optical brighteners, such as the various triazinyl stilbene and diaminostilbenedisulfonic acid compounds known in the art, including those described in EP-A-0 488 217, US-A-4,232,112, Japanese Kokai 8-202003, and Japanese Kokai 8-220715, as well as others known in the art. Two preferred optical brighteners are those commercially available as BLANKOPHOR REU™ (Mobay) and TINOPAL SFP™ (Ciba-Geigy).

The color developer composition is preferably formulated and used as an aqueous solution (concentrated or working strength), either as the working developer solution or a replenishing solution. However, as is known in the art, color developer composition can also be formulated as used as dry tablets, granules or powders, and added to the working solution or replenisher in that form. The technology for this embodiment is readily known in the art, such as US-A-5,362,610, US-A-5,376,509 and EP-A 0 611 986A1.

The color developer composition of this invention has obvious utility to provide color development in an imagewise exposed color photographic materials comprising a support and one or more silver halide emulsion layers containing an imagewise distribution of developable silver halide emulsion grains to provide one or more color records. A wide variety of types of photographic elements (both color negative and reversal films, and color papers) containing various types of emulsions can be processed using the present invention, the types of elements being well known in the art (see *Research Disclosure*, noted above). In particular, the invention can be used to process color photographic papers of all types of emulsions, including so-called "high chloride" and "low chloride" type emulsions, and so-called tabular grain emulsions as well. The color developer composition can also be used in color reversal processing.

The present invention is particularly useful to process high chloride (greater than 70 mol % silver chloride and preferably greater than 90 mol % silver chloride) emulsions in color photographic papers comprising a reflective support (usually a resin-coated paper containing reflective pigments) and two or more color records. In such instances, the amount of silver iodide in the noted emulsion layer is generally less than 1 mol %.

Such color photographic papers can have any useful amount of silver coated in the one or more emulsions layers, and in some embodiments, low total silver elements (that is, having less than a total of 0.8 g Ag/m<sup>2</sup>, for example from 0.3 to 0.7 g Ag/m<sup>2</sup>) are processed with the present invention. In some embodiments, it may be useful to incorporate the dye forming couplers described herein in a green light recording unit, or a single green-light sensitive layer, that contains less than 0.25 g Ag/m<sup>2</sup> (and preferably from 0.06 to 0.2 g Ag/m<sup>2</sup>).

The layers of the photographic elements can have any useful binder material or vehicle as it known in the art, including various gelatin and other colloidal materials. One useful binder material is acid processed gelatin which can be present in any layer in any suitable amount.

The photographic elements processed in the practice of this invention can be single or multilayer color elements. Multilayer color elements typically contain dye image-forming units sensitive to each of the three primary regions of the visible spectrum. Each unit can be comprised of a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element can be arranged in any of the various orders known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer. The elements can also contain other conventional layers such as filter layers, interlayers, subbing layers, overcoats and other layers readily apparent to one skilled in the art. A magnetic backing can be used as well as conventional supports.

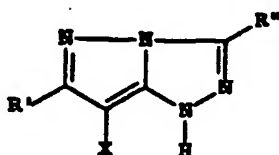
Considerable details of element structure and components, and suitable methods of processing various types of elements are described in *Research Disclosure*, noted above. Included within such teachings in the art are the use of various classes of cyan, yellow and magenta color couplers (including pyrazolotriazole magenta dye forming couplers in addition to those described below) which can be used with the present invention. These various other classes of cyan, yellow and magenta color couplers may also provide, in combination with the hydroxylamine derivatives described herein, increased  $D_{\max}$  in dye density in specific dye forming layers. In addition, the present invention can be used to process color photographic papers having pigmented resin-coated paper supports which are prepared with the

usual internal and external sizing agents (including alkylketene dimers and higher fatty acids), strengthening agents and other known paper additives and coatings.

Useful color photographic papers that can be used in the practice of this invention include, but are not limited to, KODAK EKTACOLOR EDGE® 5 Paper, KODAK EKTACOLOR PORTRA® III Paper, AGFACOLOR PROFESSIONAL SIGNUM Paper, AGFACOLOR Paper Type 10, FUJICOLOR SUPER FA Type P Paper, KONICA COLOR QA Paper Type A6 and KONICA COLOR QA Paper Professional Type P5.

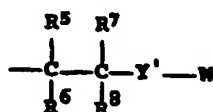
The particular advantages described above relating to increased dye density are especially evident when the color developer compositions described herein are used to process color silver halide photographic elements, such as color silver halide photographic papers, that contain one or more magenta dye-forming couplers as described below, such couplers being in or associated with one or more green light sensitive silver halide emulsion layers, such couplers being defined as having the following formula II:

The invention provides a photographic element comprising a silver halide emulsion layer having associated therewith a dye-forming coupler represented by formula II:



wherein

X is hydrogen or a coupling-off group; and  
R' is a tertiary alkyl group and R'' represents the group



wherein R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently hydrogen or alkyl groups, and any two of R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> can be joined together to form a ring.

R<sup>8</sup> is hydrogen or a substituent, provided that R<sup>7</sup> and R<sup>8</sup> may join to form a ring when R<sup>8</sup> is a substituent.

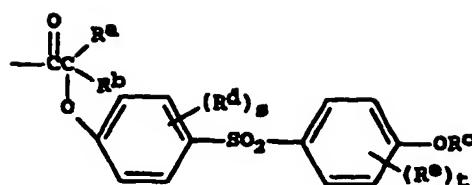
Y' is either -NH- or -CH<sub>2</sub>-, and is preferably -NH-. One or more hydrogen atoms of the Y' groups can be substituted with an alkyl group having 1 or 2 carbon atoms, if desired.

W is a substituent selected from the group consisting of -C(O)R<sup>9</sup>, -SO<sub>2</sub>R<sup>9</sup>, and -P(O)(OR<sup>10</sup>)<sub>2</sub> in which R<sup>9</sup> is selected from the group consisting of alkyl, aryl, alkoxy, aryloxy, alkylamino, and arylamino groups and R<sup>10</sup> is selected from the group consisting of alkyl and aryl groups. Examples of such groups include, but are not limited to, amide groups, carbamate groups, and urea groups as well as sulfonamides and phosphonamides. In one embodiment, W contains the substituent group -NHC(O)R<sup>11</sup> or -NHSO<sub>2</sub>R<sup>11</sup> where R<sup>11</sup> is an alkyl or aryl group.

R<sup>9</sup> is an alkyl, aryl, alkoxy, aryloxy, alkylamino, or arylamino group. Such groups typically have up to 40 carbon atoms. Examples include undecyl, ethylhexyl, isobutyl, and 2-aryloxytridecyl groups. The alkoxy group can contain up to 40 carbon atoms and be derived from methanol, ethanol, *t*-butanol, dodecanol or 2-aryloxyethanol. Suitable examples of aryl groups include those listed for R<sup>8</sup>. Suitable aryloxy groups include phenols such as 2,4-di-*t*-pentylphenoxy and naphthols. Alkylamino groups include aliphatic amines such as butylamine and dodecylamine as well as anilines including *p*-dodecylanilines. Preferably, R<sup>9</sup> is an alkyl group, and more preferably, it contains a hetero atom located  $\alpha$  to the carbon of R<sup>9</sup> bonded to -C(O)- or -SO<sub>2</sub>-.

R<sup>10</sup> is more narrowly defined than R<sup>9</sup> and extends only to alkyl and aryl groups with examples as indicated above.

In a preferred sub-class of dye-forming couplers useful in this invention, represented by formula II, W is defined as a particular -C(O)R<sup>9</sup> group, that is, a substituent having the formula III:



wherein  $R^a$  and  $R^b$  are independently selected from the group consisting of hydrogen, and alkyl or aryl groups,  $R^c$  is a substituent, each  $R^d$  and  $R^e$  is an independently selected substituent, and  $s$  and  $t$  are independently selected integers of from 0 to 4.

More specifically,  $R^a$  and  $R^b$  are independently selected from hydrogen, alkyl groups or aryl groups. Suitably,  $R^a$  will be a alkyl or aryl group, conveniently an alkyl group and  $R^b$  will be hydrogen, or an alkyl or aryl group. Suitably  $R^a$  and  $R^b$  are independently selected from a phenyl group or an alkyl group having up to 30 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, octyl, decyl, hexadecyl, and so forth  $R^a$  is one possible location for a ballast group which will serve to render the coupler nondiffusing in the emulsion layer. For this purpose, the alkyl group will typically contain at least 6 or more carbon atoms. It is provided that  $R^a$  and  $R^b$  may join to form a ring such as a cyclopentyl ring.

$R^c$  is a substituent and is suitably an alkyl or aryl group. Arylalkyl groups such as phenylmethylene groups are useful. If desired, this group may perform some or all of the ballasting required of the coupler. If it supplies all of the ballast it will contain 6 or more carbon atoms and suitably 10 or more carbon atoms.

Each  $R^d$  and  $R^e$  is an independently selected substituent with  $s$  and  $t$  being independently selected integers from 0 to 4. Examples of suitable substituents are alkyl, aryl, alkoxy, aryloxy and halogen groups.

The  $R^a$  through  $R^e$  substituents may also be selected so as to improve the activity of the coupler. Solubilizing groups such as hydroxyl, sulfonamide, and carboxyl groups are examples of suitable such groups.

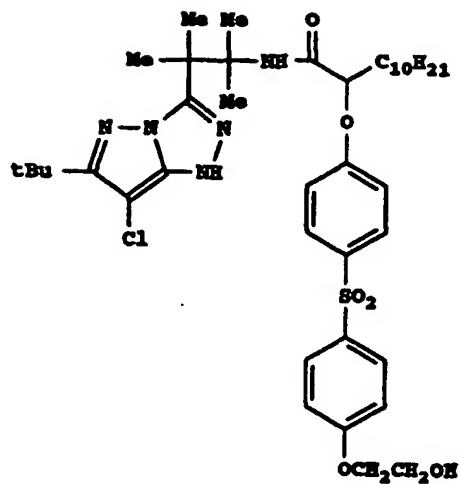
The magenta dye-forming couplers useful in this invention are termed 1H-pyrazolo[5,1-c]-1,2,4-triazole compounds. Substituent  $R^1$  of the coupler is suitably any tertiary alkyl group. Suitable examples include 1-methyl-1-cyclopropyl, *t*-butyl, *t*-octyl and adamantyl.

Preferably,  $R^5$ ,  $R^6$ , and  $R^7$  are independently selected alkyl groups. Suitably they each contain from 1 to 20 carbon atoms, often 6 or less carbons. Typically, methyl, ethyl, propyl, isopropyl or dodecyl groups are employed. It is suitable to have  $R^5$  and  $R^6$  can be joined together to form cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and so forth

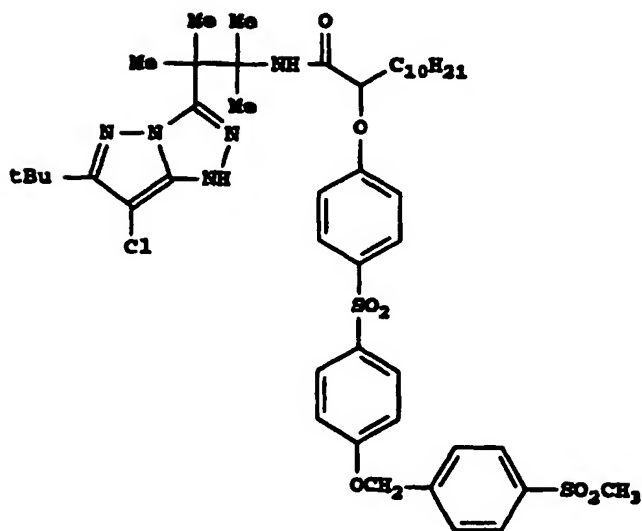
It is generally preferred that  $R^8$  be a substituent rather than hydrogen.  $R^8$  may suitably be an alkyl, aryl or a heterogroup. Suitably,  $R^8$  will have from 1 to 20 carbon atoms and is preferably an alkyl group. Also useful are phenyl groups such as phenyl, methoxyphenyl, methylsulfonamidophenyl, or tolyl and naphthyl groups.

In one embodiment of the invention,  $R^5$  through  $R^8$  are each independently selected unsubstituted alkyl groups. In another embodiment they are each unsubstituted methyl groups.

The following are examples of couplers useful in the invention (hereinafter, "tBu" represents tertiary butyl, "Et" represents ethyl, "Me" represents methyl, and "Ac" represents acetyl.). Among these compounds, M-29, M-37, M-39 and M-66 are more preferred, and M-29 is most preferred.



M-1



M-2



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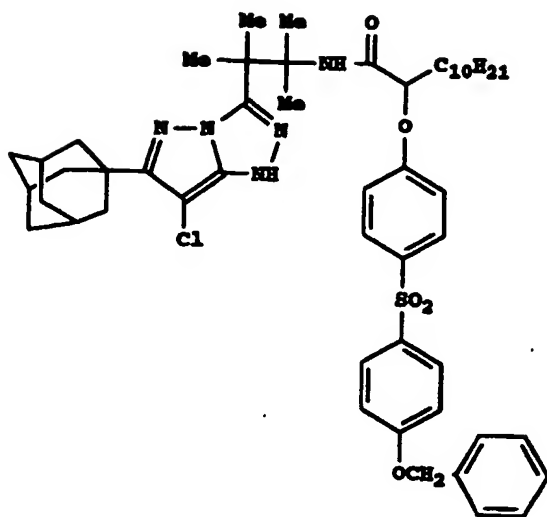
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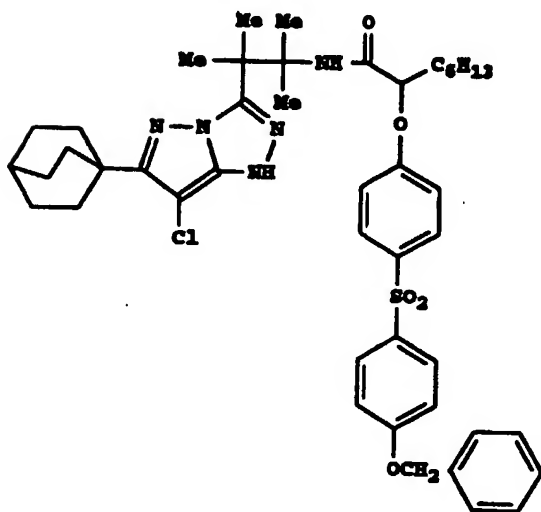
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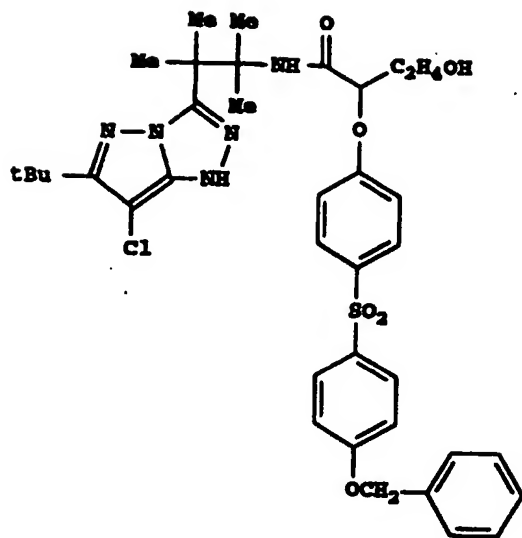
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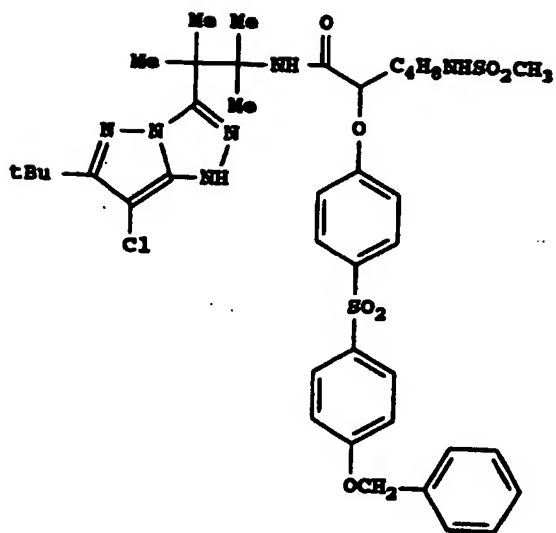
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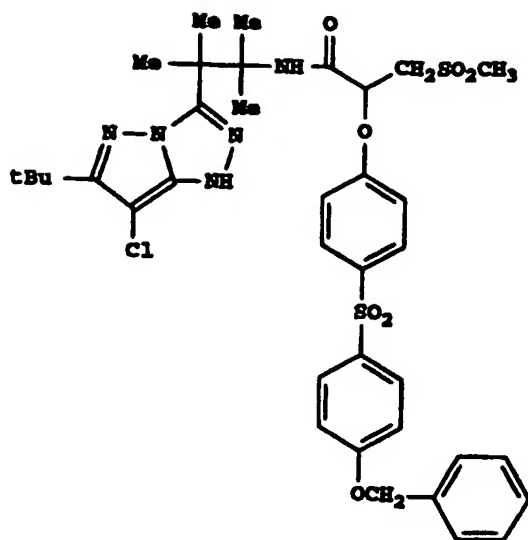
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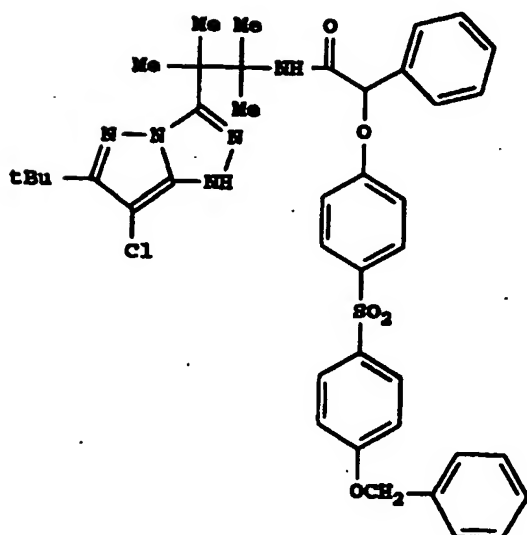
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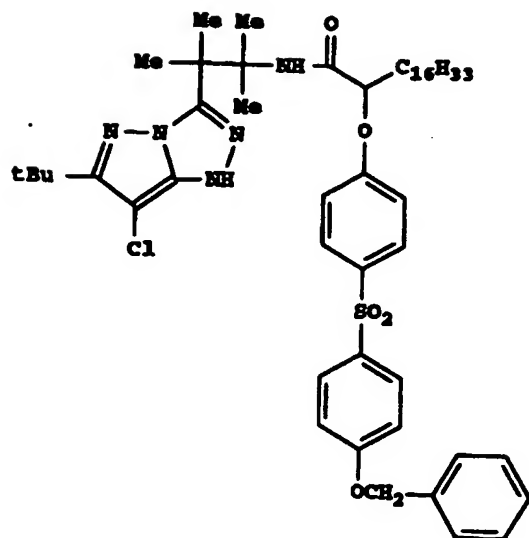
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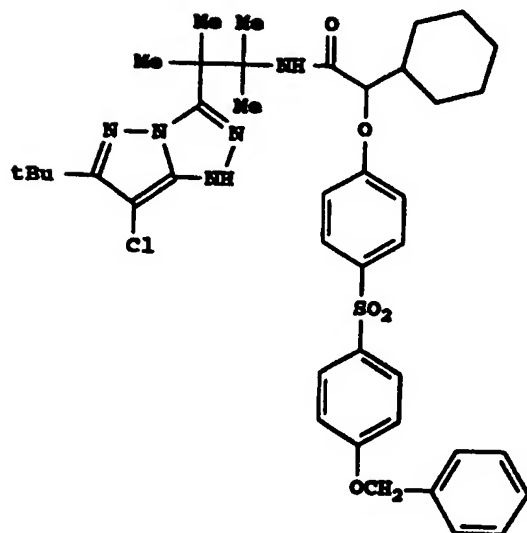
M-7



M-8



M-9



M-10

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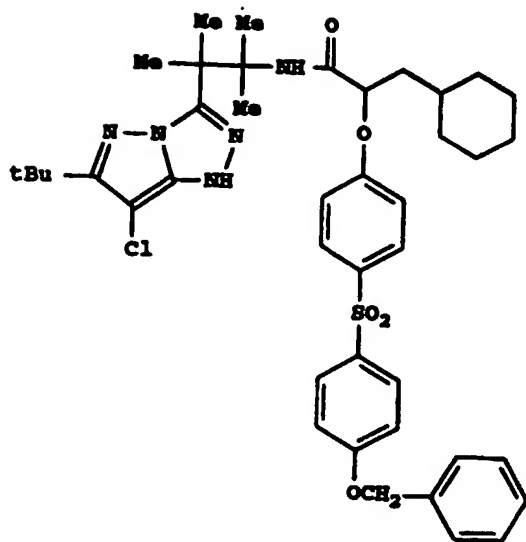
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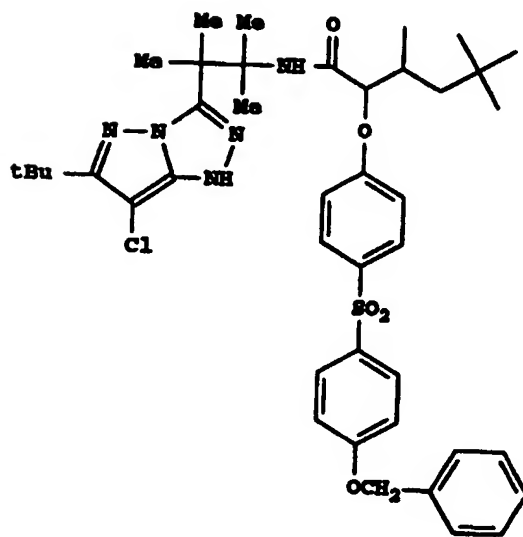
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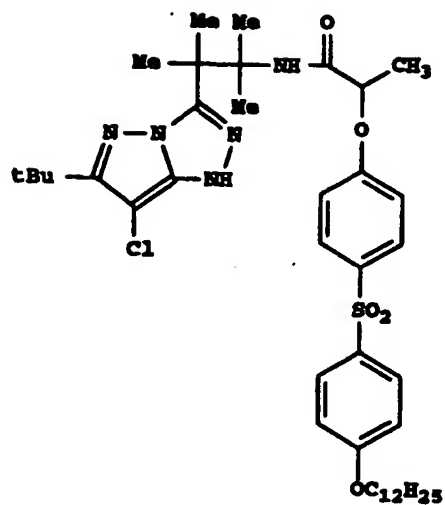
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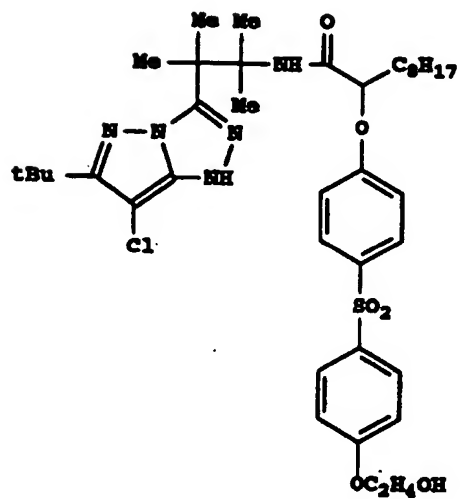
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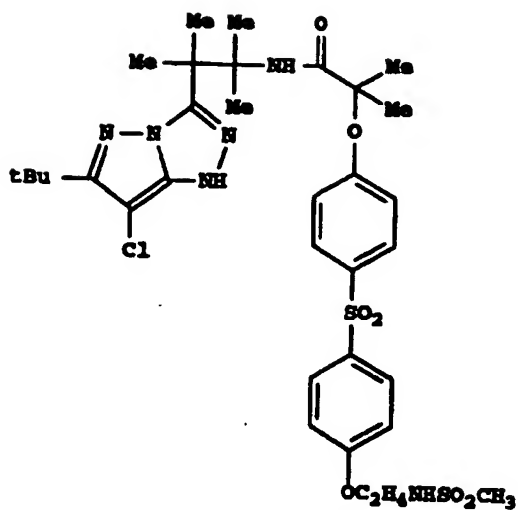
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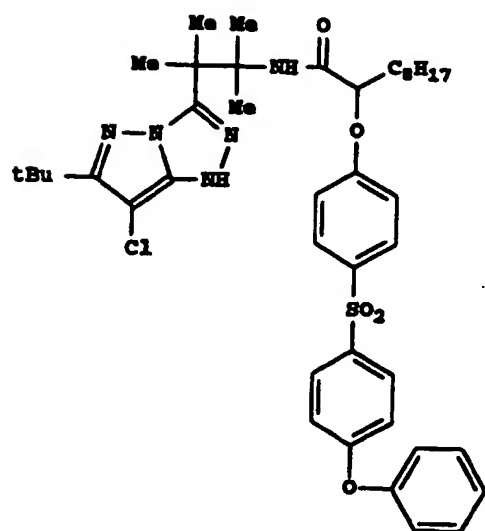
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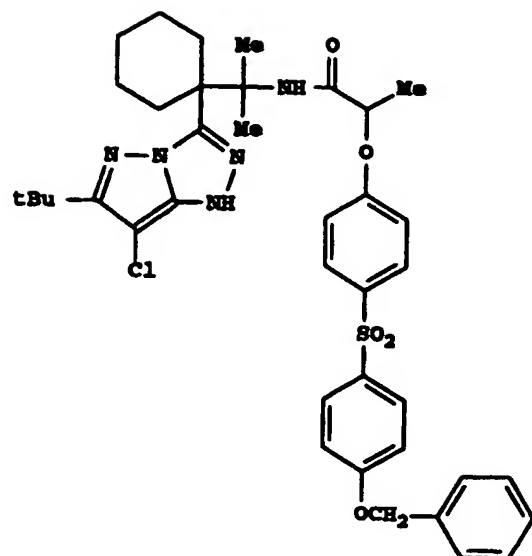
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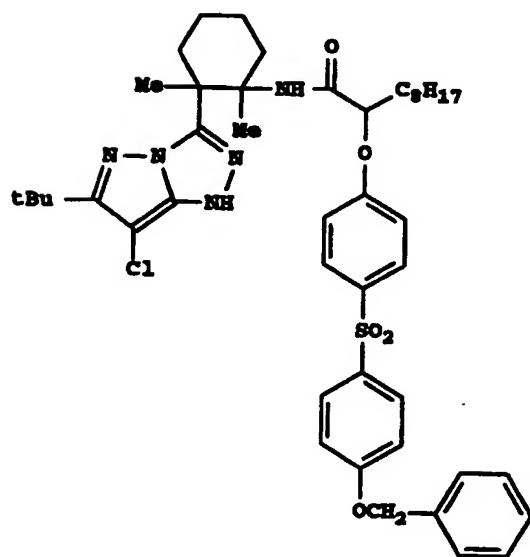
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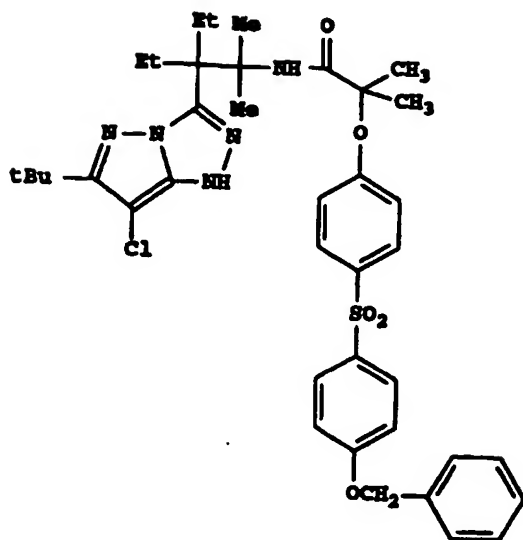


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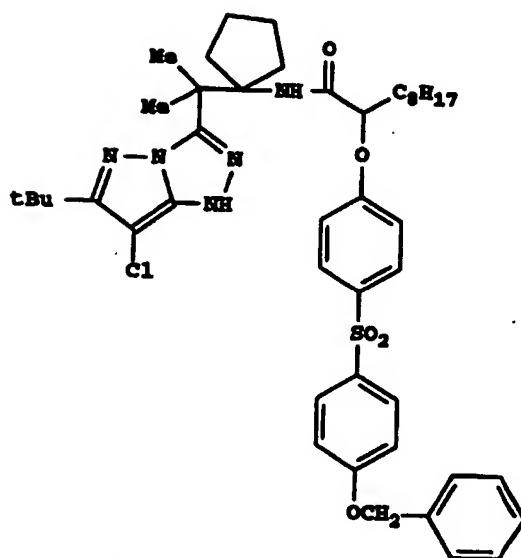


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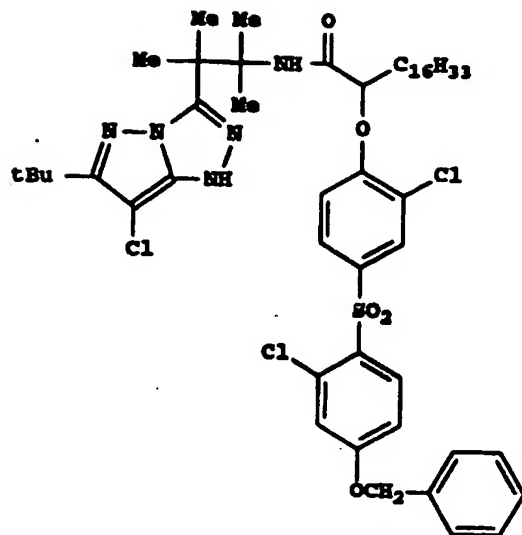




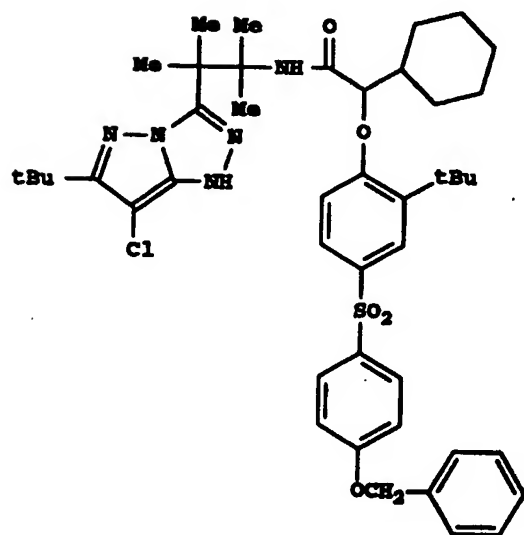
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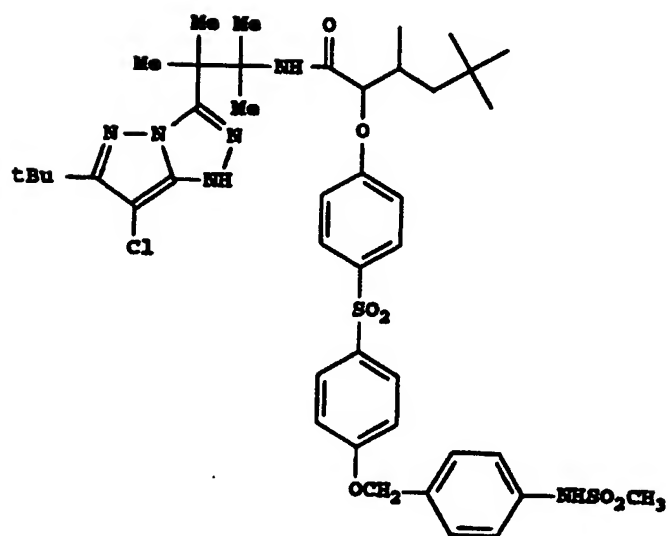
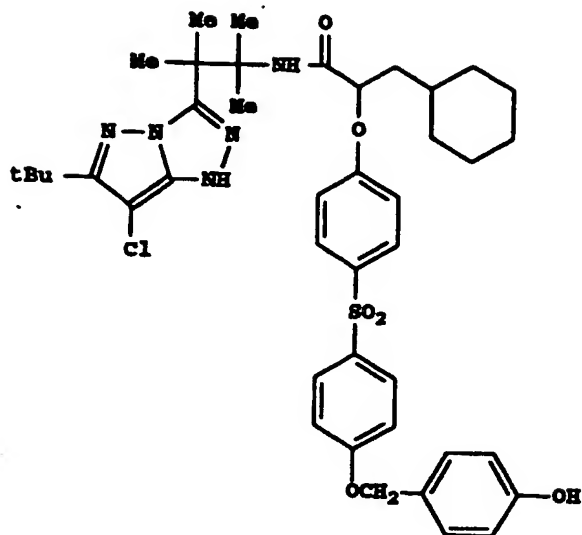
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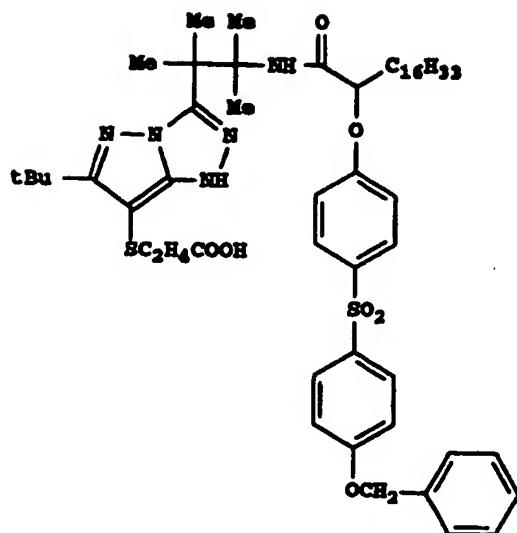


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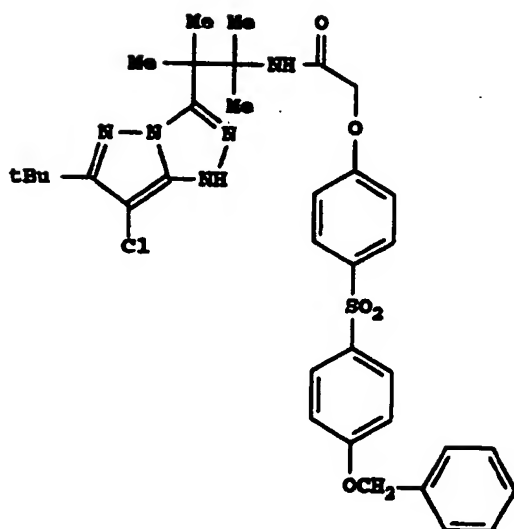


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M-25



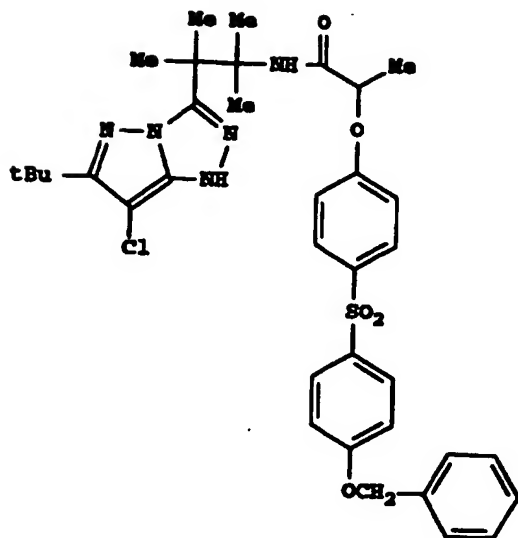
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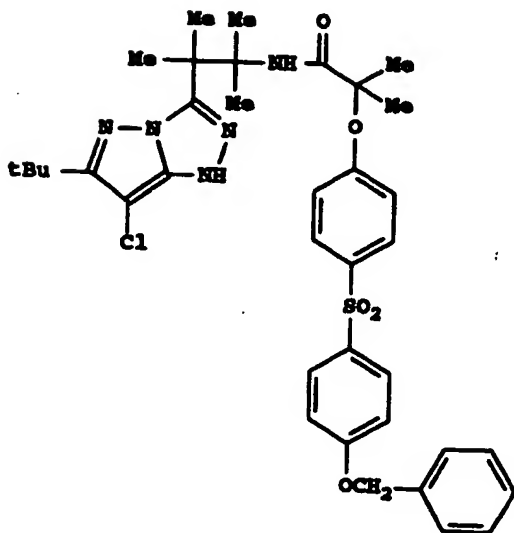
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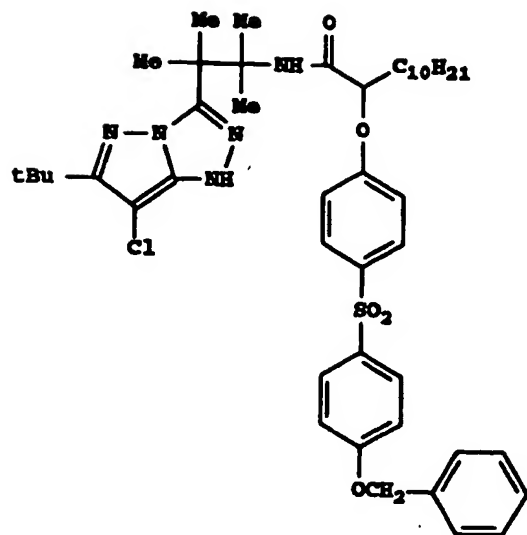


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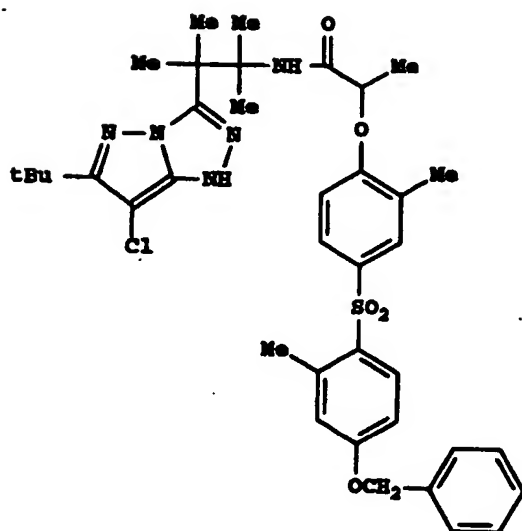
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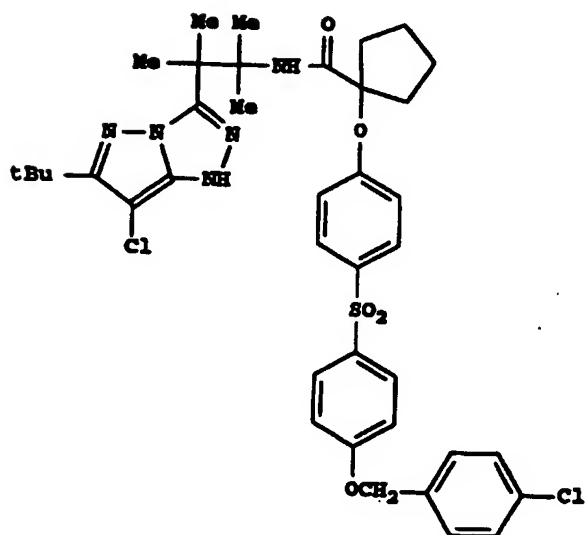
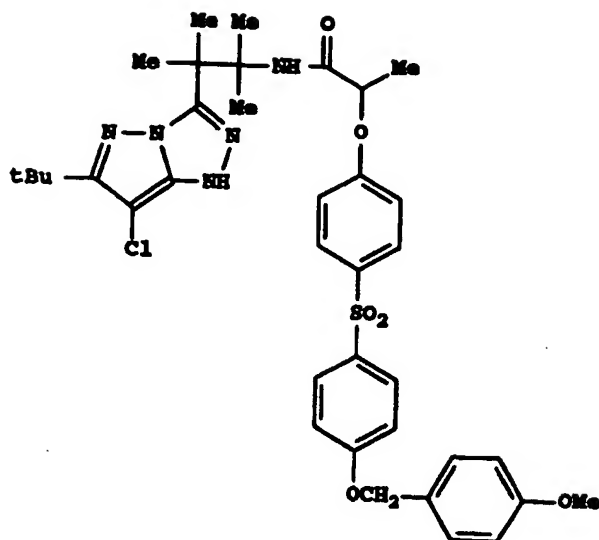
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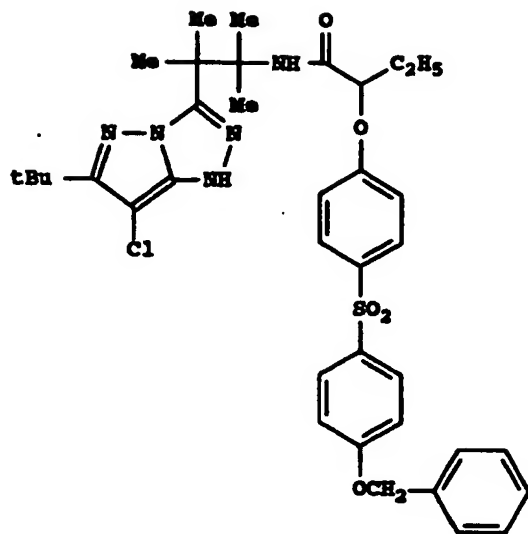


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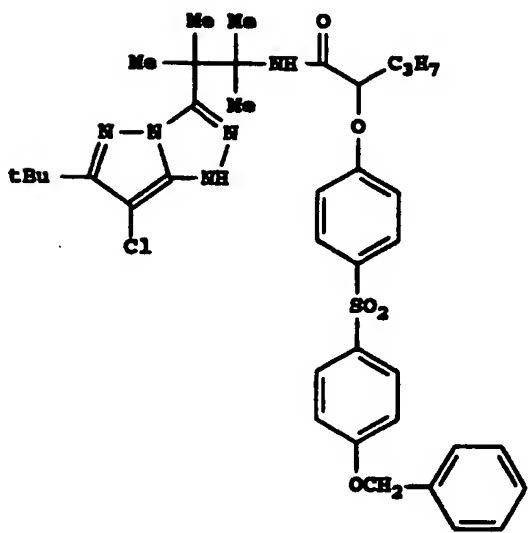


M-30





M-33



M-34

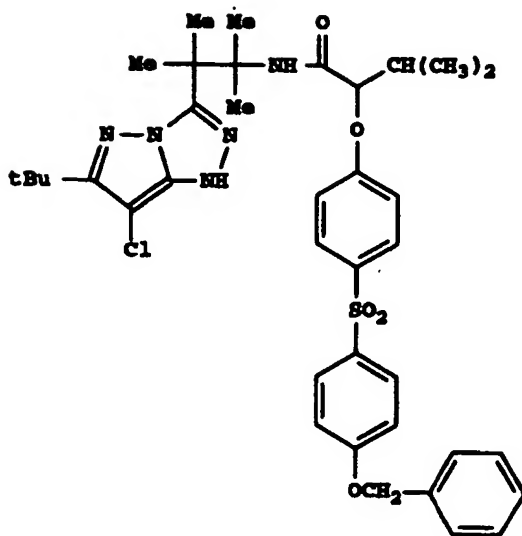


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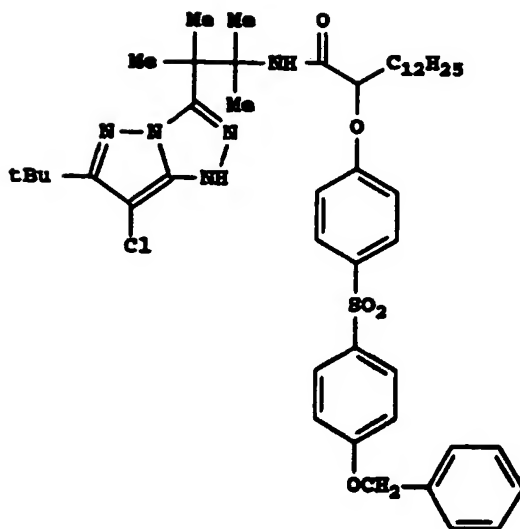
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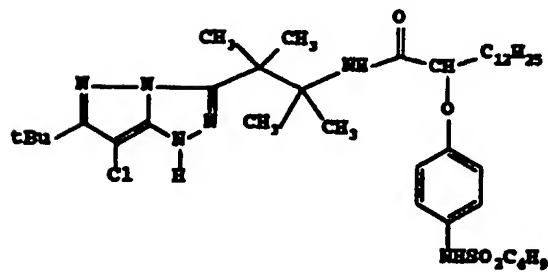


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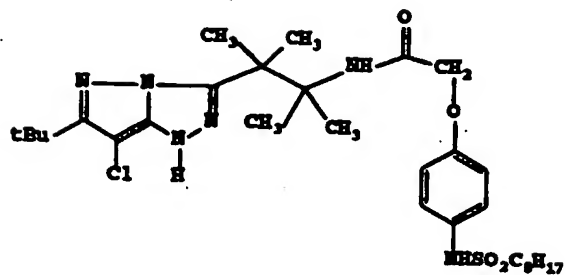
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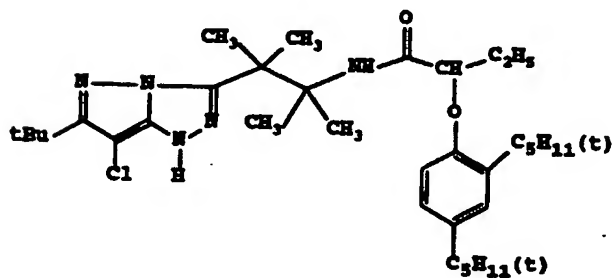
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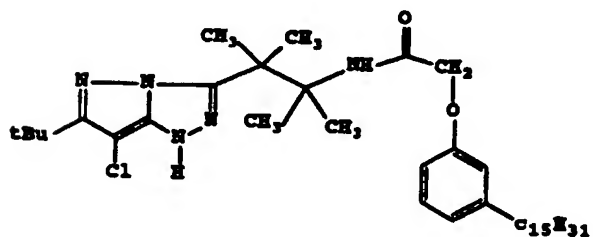
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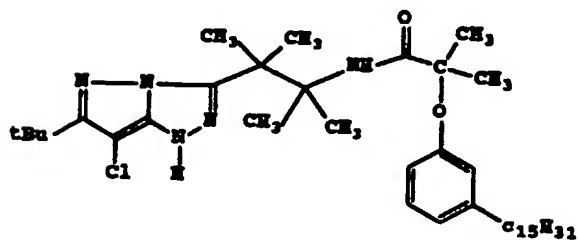
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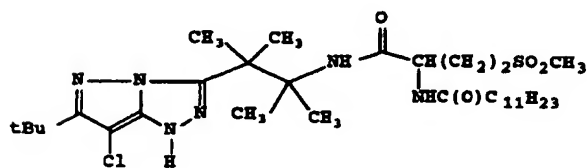
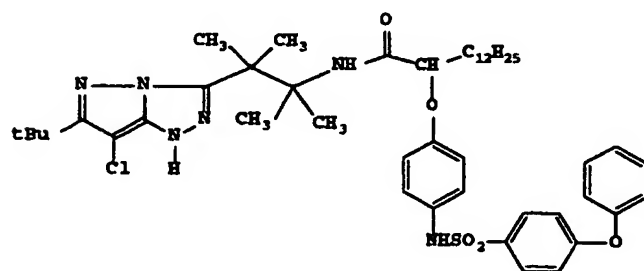
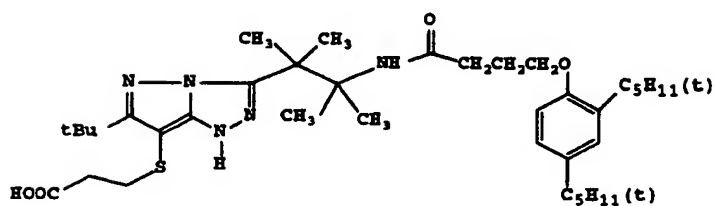
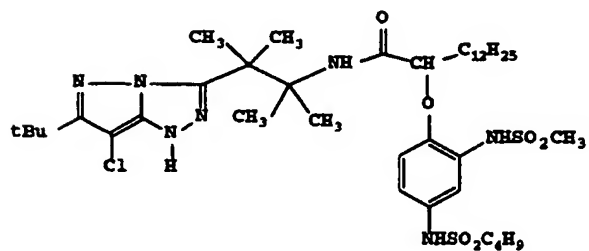
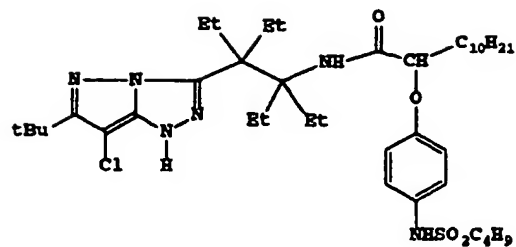
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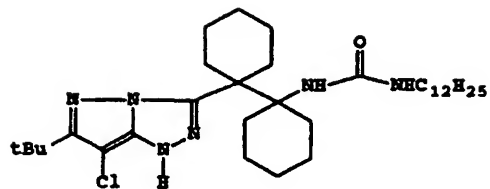


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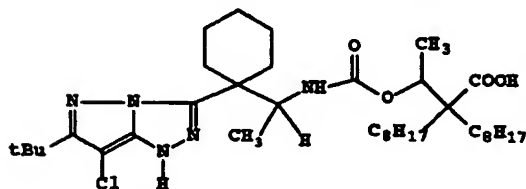


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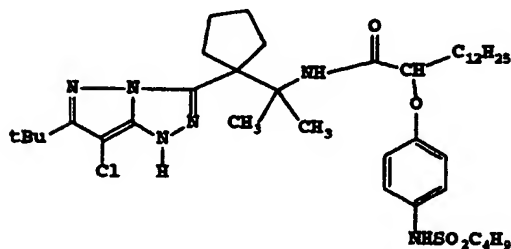




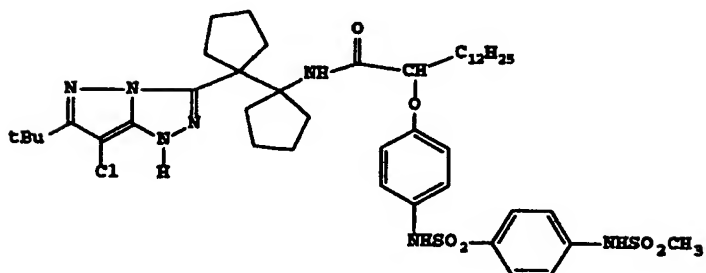
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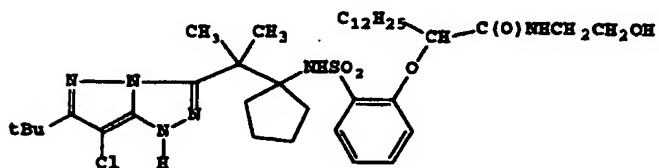
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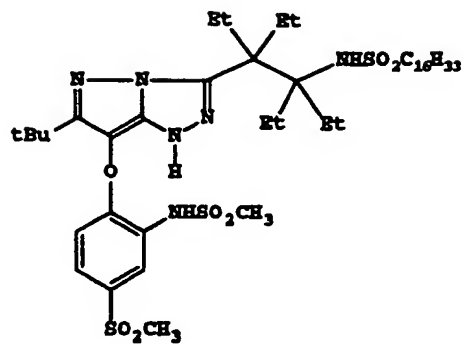
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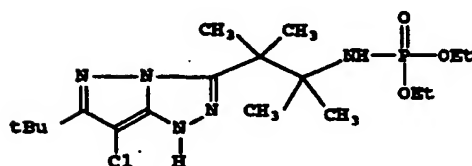
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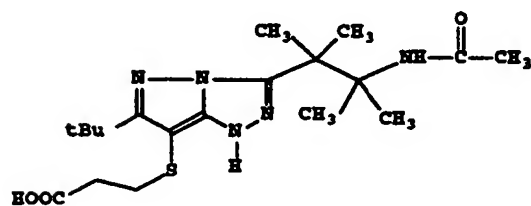
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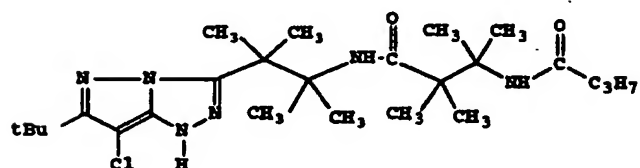
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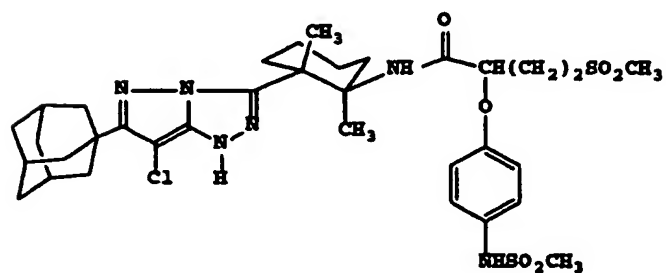
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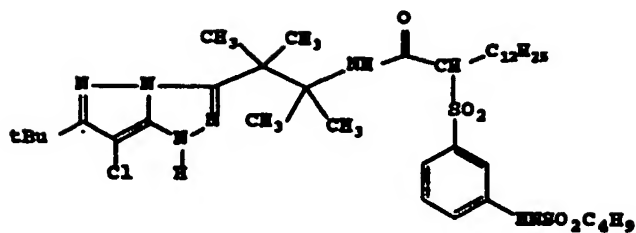
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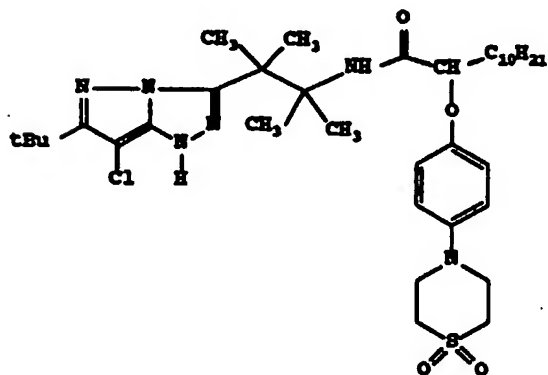
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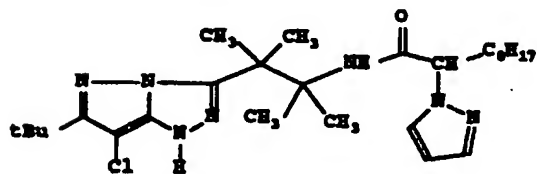
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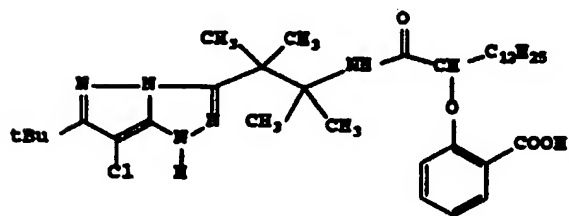
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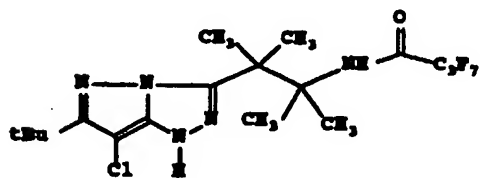
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M-59



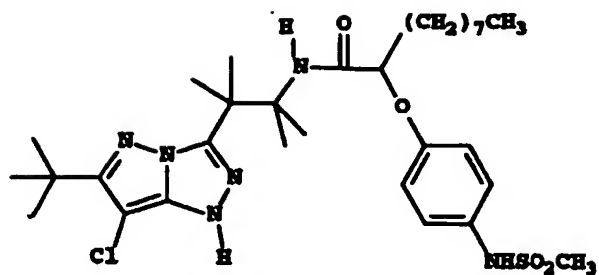
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M-61

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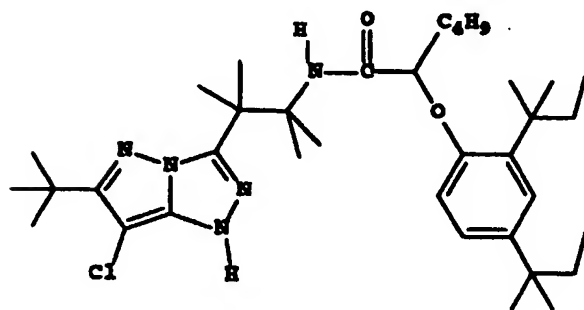
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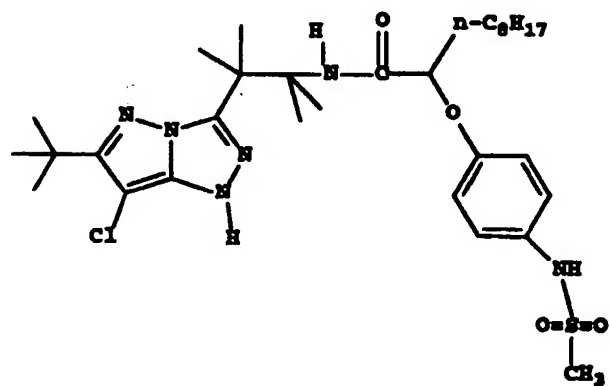


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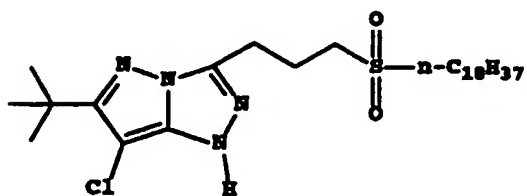
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representative patents and publications as: US-A-2,298,443, US-A-2,407,210, US-A-2,875,057, US-A-3,048,194, US-A-3,265,506, US-A-3,447,928, US-A-4,022,620, US-A-4,443,536, and "Farbkuppler-eine Literaturübersicht," published in *Agfa Mitteilungen*, Band III, pp. 112-126 (1961). Such couplers are typically open chain ketomethylene compounds.

Any of the foregoing couplers are likely to show an increase in  $D_{\max}$  in the practice of the present invention when used in combination with the noted hydroxylamine derivatives.

Couplers that form colorless products upon reaction with oxidized color developing agent are described in such representative patents as: GB-861,138, US-A-3,632,345, US-A-3,928,011, US-A-3,958,993 and US-A-3,961,959. Typically such couplers are cyclic carbonyl containing compounds that form colorless products on reaction with an oxidized color developing agent

Couplers that form black dyes upon reaction with oxidized color developing agent are described in such representative patents as US-A-1,939,231, US-A-2,181,944, US-A-2,333,106, and US-A-4,126,461, DE-2,644,194 and DE-2,650,764. Typically, such couplers are resorcinols or m-aminophenols that form black or neutral products on reaction with oxidized color developing agent

In addition to the foregoing, so-called "universal" or "washout" couplers may be employed. These couplers do not contribute to image dye-formation. Thus, for example, a naphthol having a unsubstituted carbamoyl or one substituted with a low molecular weight substituent at the 2- or 3- position may be employed. Couplers of this type are described, for example, in US-A-5,026,628, US-A-5,151,343, and US-A-5,234,800.

It may be useful to use a combination of couplers any of which may contain known ballasts or coupling-off groups such as those described in US-A-4,301,235; US-A-4,853,319 and US-A-4,351,897. The coupler may contain solubilizing groups such as described in US-A-4,482,629.

The magenta dye-forming couplers described herein can be incorporated into one or more silver halide emulsion layers (typically those sensitive to green light), alone or in combination, in suitable amounts. Generally, such amounts are at least 0.0001 mol/m<sup>2</sup> and preferably from 0.0002 to 0.0008 mol/m<sup>2</sup>.

To further enhance the light stability of the dyes formed from the couplers described herein, it is generally desired to include one or more stabilizing compounds as are known in the art, including those described in U.S.S.N. 08/610,198 noted above.

Typically, the dye-forming couplers and the stabilizers with which they are associated are dispersed in the same silver halide emulsion layer of the photographic element in a high boiling organic compound known in the art as a coupler solvent. Representative coupler solvents include phthalic acid alkyl esters such as diundecyl phthalate, dibutyl phthalate, bis-2-ethylhexyl phthalate, and dioctyl phthalate, phosphoric acid esters such as tricresyl phosphate, diphenyl phosphate, tris-2-ethylhexyl phosphate, and tris-3,5,5-trimethylhexyl phosphate, citric acid esters such as tributyl acetylitate, 2-(2-butoxyethoxy)ethyl acetate, and 1,4-cyclohexyldimethylene bis(2-ethylhexanoate), benzoic acid esters such as octyl benzoate, aliphatic amides such as N,N-diethyl lauramide, N,N-diethyldodecanamide, N,N-dibutyldodecanamide, mono- and polyvalent alcohols such as oleyl alcohol and glycerin monooleate, and alkyl phenols such as *p*-dodecyl phenol and 2,4-di-*t*-butyl or 2,4-di-*t*-pentyl phenol. Commonly used coupler solvents are the phthalate esters, which can be used alone or in combination with one another or with other coupler solvents. Selection of the particular coupler solvent has been found to have an influence both on the activity of the coupler and the hue of the dye formed on coupling. Diundecyl phthalate, dibutyl phthalate and oleyl alcohol are most preferred coupler solvents.

Generally, the amount of coupler solvent in a given silver halide emulsion layer can vary widely depending upon the amount and type of coupler, and other factors known by a skilled artisan, but is usually at least 0.06 g/m<sup>2</sup>, and preferably is from 0.1 to 0.4 g/m<sup>2</sup> for the magenta dye forming couplers described herein.

Unless otherwise specifically stated, substituent groups which may be substituted on antioxidant or coupler molecules described herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for photographic utility. When the term "group" is applied to the identification of a substituent containing a substitutable hydrogen, it is intended to encompass not only the substituent's unsubstituted form, but also its form that is further substituted with any group or groups as herein mentioned. Suitably, the group may be halo or may be bonded to the remainder of the molecule by a atom of carbon, silicon, oxygen, nitrogen, phosphorous, or sulfur. The substituent may be, for example, halo (such as chloro, bromo or fluoro), nitro, hydroxyl, cyano, carboxyl, or groups which may be further substituted, such as alkyl, including straight or branched chain alkyl (such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-pentylphenoxy) propyl, and tetradecyl], alkenyl (such as ethylene and 2-butene), alkoxy (such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy and 2-dodecyloxyethoxy), aryl (such as phenyl, 4-*t*-butylphenyl, 2,4,6-trimethylphenyl and naphthyl), aryloxy (such as phenoxy, 2-methylphenoxy,  $\alpha$ - or  $\beta$ -naphthylloxy and 4-tolyloxy), carbonamido [such as acetamido, benzamido, butyramido and tetradecanamido,  $\alpha$ -(2,4-di-*t*-pentyl-phenoxy)acetamido,  $\alpha$ -(2,4-di-*t*-pentylphenoxy)butyramido,  $\alpha$ -(3-pentadecylphenoxy)-hexanamido and  $\alpha$ -(4-hydroxy-3-*t*-butylphenoxy)tetradecanamido], 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzoyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-*t*-butylphenoxy carbonylamino,

phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecylphenylcarbonylamino, *p*-toluylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-dioctadecylureido, N,N-dioc-  
 5 tyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-*p*-toluylureido, N-(*m*-hexadecylphenyl)ureido, N,N-(2,5-di-*t*-pentylphenyl)-N'-ethylureido, and *t*-butylcarbonamido, sulfonamido (such as methylsulfonamido, benzenesul-  
 fonamido, *p*-toluylsulfonamido, *p*-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropylsulfamoylamino and hexadecylsulfonamido), sulfamoyl (such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-  
 dipropylsulfamoyl, N-hexadecylsulfamoyl and N,N-dimethylsulfamoyl), N-[3-(dodecylloxy)propyl]sulfamoyl, N-[4-(2,4-di-  
 10 *t*-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl, carbamoyl (such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, N-  
 methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl), acyl (such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, phenox-  
 ycarbonyl, *p*-dodecylphenoxy carbonyl methoxycarbonyl, butoxycarbonyl, tetradecylloxycarbonyl, ethoxycarbonyl,  
 benzylloxycarbonyl, 3-pentadecylloxycarbonyl, and dodecylloxycarbonyl), sulfonyl (such as methoxysulfonyl, octylloxysul-  
 15 fonyl, tetradecylloxysulfonyl, 2-ethylhexylloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxy sulfonyl, methylsulfonyl,  
 octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl and *p*-  
 toluylsulfonyl), sulfonyloxy (such as dodecylsulfonyloxy and hexadecylsulfonyloxy), sulfinyl (such as methylsulfinyl,  
 octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl and *p*-toluyl-  
 sulfinyl), thio (such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-  
 20 butoxy-5-*t*-octylphenylthio and *p*-tolylthio), acyloxy (such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamido-  
 benzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbamoyloxy), amine (such as phenylanilino,  
 2-chloroanilino, diethylamine or dodecylamine), imino (such as 1-(N-phenylimido)ethyl, N-succinimido or 3-benzylthi-  
 dantoinyl), phosphate (such as dimethylphosphate and ethylbutylphosphate), phosphite (such as diethyl and dihexyl-  
 phosphite), a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be  
 substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero  
 atom selected from the group consisting of oxygen, nitrogen and sulfur, such as 2-furyl, 2-thienyl, 2-benzimidazolylloxy  
 25 or 2-benzothiazolyl, quaternary ammonium, such as triethylammonium, and silyloxy (such as trimethylsilyloxy).

If desired, the substituents may themselves be further substituted one or more times with the described substituent  
 groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic  
 properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking  
 groups, releasing or releasable groups, and so forth. Generally, the above groups and substituents thereof may include  
 30 those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater  
 numbers are possible depending on the particular substituents selected.

The materials of the invention can be used in any of the ways and in any of the combinations known in the art. Typ-  
 ically, the invention materials are incorporated in a silver halide emulsion and the emulsion coated as a layer on a sup-  
 port to form part of a photographic element. Alternatively, unless provided otherwise, they can be incorporated at a  
 35 location adjacent to the silver halide emulsion layer where, during development, they will be in reactive association with  
 development products such as oxidized color developing agent. Thus, as used herein, the term "associated" signifies  
 that the compound is in the silver halide emulsion layer or in an adjacent location where, during processing, it is capable  
 of reacting with silver halide development products.

To control the migration of various components, it may be desirable to include a high molecular weight hydrophobe  
 40 or "ballast" group in coupler molecules. Representative ballast groups include substituted or unsubstituted alkyl or aryl  
 groups containing 8 to 42 carbon atoms. Representative substituents on such groups include alkyl, aryl, alkoxy, aryloxy,  
 alkylthio, hydroxy, halogen, alkoxy carbonyl, aryloxy carbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, car-  
 bamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido, and sulfamoyl groups wherein the substituents typically contain 1 to 42  
 carbon atoms. Such substituents can also be further substituted.

The photographic elements are typically exposed to suitable radiation to form a latent image and then processed  
 45 to form a visible dye image using the present invention. Processing includes the step of color development to reduce  
 developable silver halide and to oxidize the color developing agent as described below. Additional processing steps can  
 then be carried out using conventional procedures, including but not limited to, one or more development stop, bleach-  
 ing, fixing, bleach/fixing, washing (or rinsing), stabilizing and drying steps, in any particular desired order as would be  
 50 known in the art. Useful processing steps, conditions, materials and amounts useful therefor are well known (see for  
 example, *Research Disclosure* and references cited therein). It is particularly useful to use the present invention to  
 process color photographic papers using color development, bleach/fixing, and washing steps.

Processing according to the present invention can be carried out using conventional deep tanks holding processing  
 solutions. Alternatively, it can be carried out using what is known in the art as "low volume thin tank" processing sys-  
 55 tems, or LVTT, which have either a rack and tank or automatic tray design. Such processing methods and equipment  
 are described, for example, in US-A-5,436,118 and publications noted therein.

The length of time and temperatures used for each processing step of the present invention are generally those  
 conventionally used in the art. For example, color development is generally carried out at a temperature of from 20 to

65 °C (preferably from 30 to 65 °C, and more preferably from 35 to 60 °C). The overall processing time (from color development to final rinse or wash) can be from 30 seconds to 40 minutes, and each step can be from 10 to 450 seconds. Short overall processing times, that is, less than 140 seconds (and preferably, less than 90 seconds), are particularly desired for processing color photographic papers. It is also particularly desirable that the time for color development using the color developer composition described herein be less than 200 seconds, and preferably less than 90 seconds (more preferably, less than 40 seconds), but longer or shorter times may be useful under particular conditions. For processing color negative films, it is desired to have an overall process of less than 4 minutes.

One method of processing photographic color papers using this invention may be carried out using a color development step of less than 40 seconds (or even less than 25 seconds), bleach-fixing of less than 40 seconds (or even less than 25 seconds), and washing/rinsing of less than 90 seconds (or even less than 60 seconds).

Preferably, the color developer composition is supplied to a processing tank at working strength. However, it can also be supplied in concentrated liquid slurry or solid form (tablet, granules or powder.)

Replenishment of the various processing solutions useful in the method of this invention can be carried out using any suitable procedure and equipment, including the regeneration of "spent" processing solution. The replenishment rates for each solution can be any of those known in the art, and for color development, the replenishment rate is generally less than 200 ml/m<sup>2</sup> and preferably from 50 to 175 ml/m<sup>2</sup>.

Thus, in a preferred embodiment of this invention, a method of providing a color image comprises:

(A) color developing an imagewise exposed color photographic silver halide paper at a temperature of from 35 to 60 °C with a color developer composition comprising:

(a) a color developing agent present in an amount of at least 0.001 mol/l, and

(b) N-isopropyl-N-(2-ethylsulfonic acid)hydroxylamine, said hydroxylamine derivative being present in the color developer composition in an amount from 0.01 to 0.1 mol/l,

wherein said photographic color paper comprises at least one green light sensitive silver halide emulsion layer, said layer having in reactive association therewith, at least one magenta dye-forming coupler identified herein as M-29, the total silver coverage in said photographic color paper being less than 0.8 g/m<sup>2</sup>, and the silver coverage within said green light sensitive silver halide emulsion layer being less than 0.2 g/m<sup>2</sup>,

(B) bleach-fixing said photographic color paper, and

(C) washing said photographic color paper,

wherein said color development is carried out for from 5 to 30 seconds, and the total time of said method is less than 120 seconds.

The method of this invention can also be, in whole or part, a redox amplification process. The color development stage of a redox amplification process is the stage in which silver halide is developed and the resulting silver image is converted to a dye image of adequate density for imaging despite the low silver levels used. The silver may be developed separately from the amplification process. It can be developed using a black-and-white developer producing no dye image or with a developer which coincidentally produces a dye image. The former could be a black-and-white developer, for instance, hydroquinone or a developer typical of those used in color image transfer systems such as the KODAK EKTAFLEX system or chromogenic developer such as that used in the standard C41 or KODAK RA100 processes. The latter could be a color image transfer developer or a chromogenic developer. In either case the amount of dye formed is low because the silver amounts used are low.

Low dye formation is acceptable because the resulting silver image is then used to produce more oxidized developer by the action of an oxidizing agent on the catalytic surface provided by the silver image. The oxidized developer can then be used to form image dye. The extra dye formed is said to amplify or intensify the image.

The two steps of development and amplification can occur simultaneously or separately or as will be seen can occur in ways which are hybrids of the two cases, i.e., where some amplification occurs in a number of baths sometimes including the bath in which silver development occurs. In the simplest case a single bath provides both development and amplification and will be referred here as the "Developer/Amplifier" bath.

This single bath development requires the oxidizing agent and developing agent to co-exist in solution. Also, anti-oxidant species which preserve developing agent against aerial oxidation need to be included in any solution containing developer, such as solution used to replenish tanks with processing chemicals. These species also react with oxidants provided for image amplification. It is somewhat surprising that solutions with these oxidizing and reducing species present are as stable as they can be made to be in practice.

A number of solution components and aspects of solution design can be used to improve solution stability. These include metal sequestrants (EP 0 615 633), the use of high pH (EP 0 654 706), the use of phosphate and borate and silicate buffers, zinc ions, the use of hydroxylamine sulphate as the anti-oxidant/preservative agent (EP 0 654 707).

Hydroxylamine sulphate can also be used in combination with hydroxylamine sulphate derivatives to provide better protection for the developer without sacrificing the benefits of improved peroxide stability. Nitrite ion is also effective at stabilizing Devamp solutions.

Materials such as certain primary amines can be used to poison any silver deposits or other active surfaces in processing tanks so that they do not catalyze the peroxide/reducing agent reaction. Effective compounds must have a certain balance between solubility and affinity for the silver surface. They usually have to be solubilized by surfactants. The concentrations and nature of the surfactants must be such that they allow the amine to be adsorbed on the silver, while preventing the separation of the amines into another liquid phase after the solutions, either replenisher or process solutions are prepared. The use of these surfactants can result in improved cleanliness of processing equipment.

An alternative to a single solution for the development stage of a Redox process is the use of more than one solution where each solution has a more specific role. The most obvious of these is where the developer is used in a first bath followed by an amplifier bath (GB 1,514,517). The amplifier can contain essentially no developer, depending on the length of time the processed material remains in the two baths. For instance, the second bath could be very short and developer in the coatings has little time to diffuse into the solution. If some developer is transferred into this bath during processing it can be removed, for instance by the use of ion exchange resins or into liquids or onto oleophilic surfaces. This has the advantage of keeping the amplifier bath containing peroxide free of those compounds which will react with it and destabilize it. It is also reported that peroxide concentration can be measured and therefore controlled through replenishment based on such measurements (JP 06-301,177).

Alternatively, an amount of developer can be maintained in the second bath in order to provide more dye formation.

This arrangement can show advantages over a single Devamp stage, but is more complicated. The advantages can be, for instance, that the concentration of developing agent in the peroxide-containing solution can be lowered, since most of the developing agent needed for imaging can be provided by the first bath (US-A-5,324,624). Also, substances such as chloride ion which lower amplification rates, can be partly removed in the first bath thus enhancing amplification in the subsequent bath.

This last advantage can apply to the simplest of the split development schemes, namely one where two or more Devamp baths are used. The first can be used to extract most of the chloride ion and the second with lower chloride can have a higher activity. The process can be formulated to take advantage of this, for instance, by lowering developer and/or peroxide concentrations thus improving stability.

Chloride ion concentrations can be managed by replenishment so that activity can be controlled as the process proceeds through separate baths (EP 0 557 330, US-A-5,380,627).

The improvements in stability described above can be applied to the amplifier baths of split development and can in some cases apply to the amplifying baths with other functions described below.

It is possible to repeat the developer/amplifier or developer then developer/amplifier sequence (EP 0 654 706).

Another arrangement is to place the oxidizing agent in the first bath which does not contain developing agent. In this case the peroxide is carried over with the processed material into the second bath and both development and amplification occurs in the second bath. Again, some transfer of material from the first to the second bath can occur. This peroxide carry-over can be tolerated and can either be maintained by replenishment or it can be removed. Removal of peroxide from the second bath can be achieved by reaction with antioxidants. In particular, sulfite ion can be used since this co-exists with the other reducing agents and reacts quickly with peroxide thus controlling its concentration.

The use of sulfite in the bath providing most of the image formation can reduce the yield of image dye. A method which avoids this problem is to use a limited volume of liquid in a second small tank in this type of processing scheme (EP 0 636 933). The second tank contains only a small concentration of sulfite, not enough to reduce the dye yield significantly. After processing, the small solution volume is added back to a larger volume of solution from which it had been drawn. The sulfite in this larger volume is then sufficient to react with the peroxide carried in by the processed material from the first bath and can be replenished to restore its concentration.

As with conventional development it may be advantageous to add inhibiting compounds which are used particularly to control minimum densities ("antifoggants") to the amplifying baths (US-A-4,062,684, US-A-4,414,305).

Redox development is not limited by continuously reducing availability or exhaustion of silver halide as is the case with conventional development. The rate at which it proceeds at the end of a development stage is therefore usually higher than for conventional development and the extent of development, i.e., the amount of dye formed is somewhat more dependent on effects such as agitation, time and temperature. The use of timed release of inhibitors from within the paper would slow amplification down and thus improve process robustness. Such inhibitors would be typically materials used for their antifoggant behavior but would be released during the process by devices such as the use of hydrolyzable blocking groups including those whose unblocking is accelerated by the presence of nucleophiles such as peroxide or hydroxylamine.

It has been discovered that it is possible to induce a Redox reaction without adding oxidizing agents to developer solutions (EP 0 635 759). The correct anti-oxidant needs to be used and oxygen must be introduced into the solution

before or during processing.

It is also possible to avoid a Redox development but still use very small amounts of silver. This is done by performing a halogenating bleach step after a conventional development and then redeveloping the silver halide to form more dye (EP 0 620 488). The number of times this has to be performed depends on the amount of silver used.

5 The above schemes can be optionally used in combination with materials containing incorporated developing agents (US-A-5,411,840, US-A-5,210,007, US-A-4,371,609, US-A-5,215,875, JP 06-332,128; JP 07-064,259; JP 07-028,186 and JP 06-347,963. US-A-4,491,627, JP 07-028,211 and JP 06-324,447). This can be a method of keeping components separate, or can be used as a means of replenishment. Coating developing agent or a precursor for developing agent on the reverse side of the paper from the imaging side is also possible. This technique can be used with  
10 other processing chemicals.

A novel method of producing consistent results from processing in general as well as redox processes is the use of materials in solid form which can release active components into the solutions but which remain in contact with the solution so that equilibria are set up thus stabilizing the concentration of the solution species despite the fact that the chemical stability of the solution species need not be improved. This technique is different from replenishment of solutions with solids.  
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Direct replenishment by concentrates can be used in combination with redox processes. Solid replenishment of chemicals can also be applied to redox processes. The use of urea-peroxide complexes provides an example of addition of hydrogen peroxide in this way. Other chemicals can be added as solids in a variety of ways (US-A-5,328,318 and US-A-5,360,136) including coating replenishment chemicals on the back of the processed material or separate webs of material fed into the processing solutions with the processed material. Alternatively they can be added from capsules or sachets or as tablets as in the Konica "Ecotab" system.  
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Replenishment of a Split Development system, or any of the combinations of baths described here, can be with any of the techniques described above. Also, it is possible to arrange the concentrations of components in the two baths such that overflow from the second bath can, after peroxide has been removed, be used to replenish the first bath (US-A-5,358,830). Other schemes involving replenishment using overflows can be used with other baths including bleach and fix baths as will be indicated below.  
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The slow loss of chemicals due to reaction of developer components with atmospheric oxygen and carbon dioxide and even, as in the case of redox processing, due to reaction between solution components is of little consequence in LVTTs during processing of material since the consumption of chemicals by the processing is greater than by such losses and this is compensated for by replenishment. When the process is idle though, the chemical changes build up over time to significant extents and should be restored by replenishment. This time-dependent mode of replenishment of chemistry (as opposed to replenishment based on consumption by processing) is effective at maintaining processes which are used for only a small fraction of the available time. The need for this type of replenishment is reduced if solutions are at lower than working temperature. With LVTT processors, because the volumes of liquid in the processors are low, the temperature can be quickly restored if lowered in order to reduce chemical losses.  
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It is clear that redox processes, and to a lesser extent, conventional processes, are more readily maintained at a consistent level of activity if the residence time of solutions in the processing tanks is low. This is, of course why LVTTs are effective in enabling processes with significant instability. It is desirable though to reduce replenishment volumes and this normally raises the solution residence time. Again LVTTs are effective in allowing replenishment volumes to be lowered. With redox solutions however, higher replenishment rates can be advantageous in practice in providing more consistent results even in LVTTs. This is inconsistent with the need to lower replenishment volumes and therefore effluent but a technique exists for overcoming the difficulty of this conflict.  
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If the replenisher solutions are added to the processing tank at a very high rate, for example, 500 ml/m<sup>2</sup> or more, very consistent results can be achieved because variations in chemical use due to processing are small compared with the flow of chemicals through the tank. This mode of replenishment is often called "flooded" replenishment. An approximation to this is achieved with replenishment rates which are lower than for a flooded process but are higher than needed normally for minimizing effluent. For instance, they can be between 10 and 20 ml/sqft. In this case, the overflow can be fed to a separate container and stored. The collected overflow solution can then be replenished as a batch once a certain volume has been collected (US-A-5,298,932). This mode achieves an improved level of consistency due to the high through-put while still allowing low replenishment rates to be used when restoring the batch of overflow to working strength.  
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If the oxidant is removed from redox solutions they become as stable as conventional solutions because they are very similar in constitution. In fact, removal of peroxide can result in a solution which is useful as a conventional developer. Removal of peroxide can be achieved in a number of ways (US-A-5,260,184) including the use of catalytic surfaces such as platinum, electrolytic methods and chemical methods such as reaction with sulfite. Sulfite reacts relatively quickly with peroxide and the resulting sulphate is of little consequence. It is a commonly used antioxidant in developer solutions and small amounts can be of benefit. Large amounts can reduce the yield of dye from oxidized developer and thus affect photographic performance. It is important therefore to add little or no more than sufficient sulfite to the solu-  
55



tion than is necessary for reaction with the peroxide. This ensures that when the solutions with peroxide removed are to be reactivated as redox solutions, there is minimal or no loss of peroxide due to reaction with the sulfite present.

Since the amount of peroxide in a redox solution can vary (usually in concert with the antioxidant which in the case of hydroxylamine sulphate has an inhibiting effect on amplification which counteracts reductions in peroxide level, thus maintaining activity at the required level) the amount of sulfite required to exactly remove the peroxide is uncertain. The oxidation of sulfite is exothermic and the temperature rise resulting from the addition of sulfite can be used to monitor the reaction and control the amount added so that excess is not used.

When using LVTs, especially when development times are short and therefore the rate of transport of sensitized material such as color negative paper, into the solutions is fast, the temperature of the solutions can be affected by any difference in temperature between the paper and the solution. The effect can be eliminated or reduced by heating the paper before entry into the solution or by anticipating a need to increase the temperature of the solution and injecting heat into the solution when it is known that paper will be entering it.

US-A-4,529,687 teaches the use of anion exchange resins to remove bromide and iodide ions. This allows more rapid processing and/or lower replenishment rates.

The low silver levels in redox technology allows a number of choices to be made in designing the stages of the process subsequent to the development stage, the process "tail end". A variety of combinations of "stop" baths (low pH baths which stop development), bleach baths (baths which convert silver to silver halide or solubilize the silver), fixing baths (which remove silver into solution) and wash or stabilizer baths (which remove any soluble material from the coating) can be imagined. For instance, the possibility of omitting a bleaching and/or fixing operation now exist. A number of these possible configurations will be described below to illustrate this freedom of design in configuring a redox process tail end.

Herein, a bath whose main function is to remove soluble material will sometimes be referred to as a wash bath even if it is used at low rates (volume per unit area of processed material) and contains substances such as antifungal or antibacterial agents or those substances which may help to stabilize the images.

The simplest tail end which removes all the silver is a combined bleach/fix solution with no wash or stop bath before the bleach/fix bath and a wash or stabilizer bath after. With redox development stages before this bleach/fix bath, it has been observed that on seasoning of the bleach/fix bath especially when replenishment rates for this bath are low and the amounts of dissolved material carried over with the process build up, stain can increase. The bleach/fix solutions need to be formulated to prevent this and additional sulfite ion has proved effective (US-A-5,354,647).

A slightly more complicated sequence but one in which replenishment of the more expensive chemicals can be lowered involves the use of a stop bath before a bleach/fix bath. It is advantageous to add fixing agent to the first tail end bath in this case since it is very effective at stopping continued amplification when combined with low pH. Also, it is possible to use the overflow from this bath to make replenisher for the subsequent bleach/fix bath. This allows the use of a concentrated solution of the more expensive bleaching agent to be used thus lowering effluent volumes and costs of process chemicals.

It can be advantageous to separate the bleach and fix stages. This allows the omission or reduction in effectiveness of one of the stages. Elimination of the bleach step while retaining fixing removes silver halide from non-image areas and areas of partial development. The effects of retained metallic silver depend on the degree to which amplification is needed to achieve full dye density. They also depend on the amounts of silver used and on the silver halide grain size.

Redox technology with its low silver also potentially allows the fixing step to be eliminated. Undeveloped silver halide then remains in non-image areas and areas of lower than maximum densities. Because it is distributed in this anti-imagewise way the effects of density changes resulting from its presence are more severe and may or may not be tolerable, depending on the amounts involved and on the image quality requirements applied. This can be the case if either very low silver levels are used or some means of preventing the retained silver halide from causing the image to be degraded after processing can be found.

A solubilizing bleach can be used without a fix step. A rehalogenating bleach can also be used and will result in silver halide being present in image areas as well as non-image areas. In fact in this case, because no silver is removed, silver halide is present uniformly.

In these cases where silver halide is present in the image, a number of ways of reducing or eliminating any problems associated with its presence exist. Photolysis of the silver halide results in the formation of silver and therefore an increase in density. The main problem is the change in density in areas of low or no dye density rather than the small density increase occurring in image areas even if the silver halide is photolyzed extensively. This is simply because of the low image density and the sensitivity of the eye to small changes in density when they occur in one light area and not in an adjacent area. The boundary of an area of minimum density exposed to light becomes obvious even at very low silver levels such as 55 mg/m<sup>2</sup>.

One way to overcome this problem is to convert the silver halide into a stable, non absorbing material such as silver iodide. This has low sensitivity to light and is not intensely colored itself (US-A-5,246,822). Another way is to pre-empt the formation of silver by photolyzing all the silver halide as part of the process. Subsequent increases in stain can thus

be avoided (US-A-5,441,853). Also, it is possible to bleach sensitizing dye by a low intensity exposure which does not produce much photolytic silver due to the strong dependence of the photolytic process on light intensity. This eliminates the response of the emulsion to visible light and therefore avoids subsequent stain growth due to this effect

Iron based bleaches contain, not only iron but one or more ligands, all of which if contained in photographic effluent, are subject to legislation in some parts of the world. The use of peroxide or compound which provide peroxide is desirable since the by-products of their use, particularly in the case of hydrogen peroxide are relatively harmless. Peroxide based bleaches have been described (EP 0 506 909 and EP 0 540 619) which are suitable for redox processes. Stabilization of replenishment solutions has also been patented (EP 0 569 576).

It is often preferable to use a bath between the development stage and the bleach, particularly with peroxide bleaches. If so, it is preferable to use sulfite ion as this is a weak fixing agent and competes for oxidized developer. Also, sulfite does not prevent the peroxide from bleaching the silver in the subsequent peroxide bath as is the case with thiosulfate.

Low levels of silver enable other fixing agents to be used than the commonly used materials the most common of which is thiosulfate. It is for instance, possible to use sulfite ion. This has advantages in being readily oxidized by effluent treatment and does not poison redox development or inhibit bleaching by peroxide when used before baths which have these functions. An example would be when it is used before a peroxide bleach bath in order to shut off development quickly while not preventing the subsequent bleach bath from working efficiently.

The effects of accidental contamination by fixing solutions using only sulfite, on development baths is minimal since sulfite is rapidly removed by peroxide and the ability of sulfite to dissolve silver halide is insufficient under these conditions to cause silver halide fog.

Thiosulfate, however, has advantages over sulfite. It is possible to use smaller amounts and thus reduce oxygen demand in effluent and reduce costs. It is also possible to achieve more rapid development.

Mixed sulfite and thiosulfate baths are also known. Here the sulfite can not only contribute to fixing and reduce the concentration of thiosulfate needed but it can also protect the thiosulfate against oxidation by peroxide introduced from previous baths.

Baths containing thiosulfate can be used after bleaching with peroxide or any other bleaching agent.

It is also possible to use baths with multiple functions other than the combination of development and amplification, include bleaching, fixing and washing or stabilizing. Some formulations which allow multiple functions will result in the stability of the single solution being lowered relative to at least one of the separate solutions providing each function. These cases will benefit from LVTT processors because of this reduced stability.

It is possible for bleaching and amplification to occur simultaneously when using peroxide as the bleach. When used after the Developer/amplifier bath, a bleach will become seasoned with Developer/amplifier solution and the components it contains and can be formulated, particularly with respect to pH, to allow further development. This enables the Developer/amplifier to perform less than 100% of the dye forming role and therefore the Developer/amplifier stage can be made less active, thus gaining some stability, and/or shorter in time. Such a bath can be used in combination with all the development stage configurations described above. For instance, it can follow a single Developer/amplifier bath or a split developer and amplifier stage. It is also possible to achieve imaging in a single bath combining the functions of development amplification and bleaching.

It is further possible to combine the three functions of amplification bleaching and fixing in a single bath.

In a sequence involving bleaching with peroxide preceded by a fixing step silver is removed from non-image areas but is retained where development has occurred. This silver can either then be removed by a further fixing stage after bleaching, or retained in the image. In the case where a fix stage follows the bleach, the processed material contains solubilized silver in all parts of the material surface. It is possible then, to improve the removal of silver in the bath following the last fix bath by adding peroxide and chloride ion to that bath. This precipitates the silver as the chloride. Any small amount of silver precipitated in the layers of the material is largely insensitive to light reaching it since most would be trapped beneath UV absorbing layers.

The following examples are provided to illustrate the practice of this invention and not to limit it in any way. Unless otherwise indicated, percentages in the examples and preparations are by weight

#### 50 Preparation of N-Isopropyl-N-(2-carboxyethyl)-hydroxylamine:

Acrylic acid (120 g) was added to an aqueous solution of isopropylhydroxylamine (15%, 825 g) and methanol (1250 ml) at room temperature with vigorous mechanical stirring. Upon completion of the addition, the reaction solution was heated to 60 °C and maintained at that temperature overnight. Upon cooling to room temperature and concentration of the reaction solution by evaporation, a yellow oil crystallized upon standing. Isopropanol and ether were added to facilitate collection of the resulting product by suction filtration for analysis. The resulting white granular solid was dried overnight under vacuum to give 155 g.

The analyses were consistent with the desired structure. The <sup>1</sup>H NMR in dimethylsulfoxide-d<sub>6</sub> had peaks at

7.0(NOH), 2.7(isopropyl methine plus methylene group of the propionic acid moiety), 2.35(methylene of propionic acid moiety), and 0.9 ppm (two methyls of the isopropyl group). The mass spectrum was consistent with the desired compound.

#### **Preparation of N-Isopropyl-N-(2-carboxymethylene-3-propionic acid)-hydroxylamine:**

Methanol (300 ml) was added to a 15% aqueous solution of N-isopropylhydroxylamine (400 ml, 0.8 moles), followed by addition of itaconic acid (104 g, 0.8 moles) in portions as a solid. Additional methanol (100 ml) was used to rinse the itaconic acid into the flask. After all of the solid acid had dissolved, the mixture was stirred at room temperature for 6 days, and filtered to collect the resulting white solid product. This material was dried under mild vacuum to a weight of 142 g (m.p. 136-8°C). NMR analysis was consistent with the structure of the desired compound.

#### **Preparation of N-Isopropyl-N-(2-carboxyethyl)hydroxylamine, Methyl Ester:**

To a solution of 33 g (66.5 mmol) of 15% aqueous isopropylhydroxylamine (w/w) and 50 ml of methanol was added 5.4 ml (5.16 g, 60 mmol) of methyl acrylate dropwise at room temperature. The solution became warm and the flask was put into a 60 °C oil bath and stirred overnight. The reaction mixture was cooled to room temperature and the methanol was removed under reduced pressure. The aqueous solution was extracted twice with ethyl acetate (50 ml), and the extracts were dried over sodium sulfate and concentrated to give 8 g (83%) of a yellow oil. A mass spectrum analysis of the oil confirmed that the desired product was the major component of the oil. A small amount of the corresponding amine was also present. The <sup>1</sup>H NMR spectrum of the desired product in CDCl<sub>3</sub> had peaks at δ6.8(NOH), 3.55 (s,3H), 2.8(m,3H), 2.5(t,2H) and δ0.95(d,6H).

N-isopropyl-N-(2-sulfonamidoethyl)-hydroxylamine, N-isopropyl-N-(2-N',N'-dimethyl-sulfonamidoethyl)hydroxylamine, and N-isopropyl-N-(2-N',N'-diethylsulfonamidoethyl)hydroxylamine were prepared using similar conditions and slightly varying solvent mixtures of water and methanol, water and tetrahydrofuran or tetrahydrofuran and N,N-dimethylformamide.

#### **Preparation of N-Isopropyl-N-(ethanesulfonic acid)hydroxylamine:**

Isopropyl hydroxylamine (330 g of 15% in water, 0.665 mol) was combined with sodium vinylsulfonate (350 g of 25% in water, 0.665 mol) and sodium hydroxide (0.4 g, 0.01 mol). The resulting solution was refluxed for four hours, after which no starting materials were detected by thin layer chromatography. The reaction mixture was cooled to room temperature and precipitated into eight liters of stirred isopropanol. The resulting white solid was dried in a vacuum oven prior to use. <sup>1</sup>H NMR (d, ppm) 2.9-3.1 (br, CH<sub>2</sub>CH<sub>2</sub>, 4H), 2.85 (septet, *i*-Pr, 1H), 0.95(d, *i*-Pr, 6H) confirmed the structure, and ion chromatography revealed no chloride ion and 1.2% sulfate.

#### **Alternative Preparation of N-Isopropyl-N-(2-ethanesulfonic acid)hydroxylamine, Sodium Salt:**

An aqueous solution (420 ml) of vinylsulfonic acid, sodium salt (25%) was heated to reflux. While at reflux, an aqueous solution (480 g) of isopropyl hydroxylamine was linearly added over a period of two hours. During the next five hours, water (600 g) was removed linearly by distillation. After cooling the reaction solution to 20°C, isopropanol (500 ml) was added with good mechanical stirring to keep the resulting white solid suspended. This solid was collected on a sintered glass funnel, rinsed with additional fresh isopropanol (100 ml), and dried overnight at 50°C under vacuum for analysis. N-isopropyl-N-(2-ethanesulfonic acid)-hydroxylamine, sodium salt was isolated as a white powder. However, the product could have been left in the reaction solution for later use if desired.

All analyses were consistent with the structure of the desired compound. The <sup>1</sup>H NMR in D<sub>2</sub>O had peaks at 4.8(NOH), 3.2-2.9(isopropyl methine and two methylenes of the ethylsulfonato sodium salt moiety), and 1.1 ppm (two methyls of the isopropyl group). The <sup>13</sup>C NMR had peaks at 59.4, 52.4, 49.9 and 19.2 ppm. The sodium analysis was 11.5%.

#### **Color Developer Compositions:**

A preferred aqueous photographic color developer composition useful in this invention was prepared by mixing the components shown in Table I:



Table I

Component	Concentration/liter
Lithium salt of sulfonated polystyrene (30% w/w)	0.25 g
Triethanolamine (100%)	11 ml
BLANKOPHOR REU Stain Reducing Agent (Mobay Corp.)	2.3 g
N-isopropyl-N-(2-ethylsulfonic acid)hydroxylamine, sodium salt	0.05 mol
Lithium sulfate	2.7 g
1-Hydroxyethylidene-1-diphosphonic acid (60% w/w)	0.8 ml
Potassium chloride	2.8 g
Potassium bromide	0.02 g
N-[2-[(4-amino-3-methylphenyl)ethylamino]ethyl]methanesulfonamide sesquisulfate	4.85 g
Potassium carbonate, anhydrous	25 g
Water to make 1 liter of solution pH adjusted to 10.10 $\pm$ 0.05 at 25 °C	

A "Control" color developer composition was similarly prepared except that the antioxidant used was N,N-diethylhydroxylamine (0.05 mol/l).

#### Photographic Elements:

The following mono- and multicolor photographic elements were prepared and processed according to this invention, with the layers and components listed in order of top to bottom:

Photographic Element I:

## Topcoat:

Gelatin	1.08 g/m <sup>2</sup>
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## UV Absorbing Layer:

Gelatin	1.08 g/m <sup>2</sup>
---------	-----------------------

Bis(vinylsulfonylmethyl) ether	2.5 mg/m <sup>2</sup>
--------------------------------	-----------------------

TINUVIN <sup>TM</sup> 328 (Ciba-Geigy)	
--	--

optical brightener	0.643 g/m <sup>2</sup>
--------------------	------------------------

TINUVIN <sup>TM</sup> 326 (Ciba-Geigy)	
--	--

optical brightener	0.11 g/m <sup>2</sup>
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## Green-Light Sensitive Emulsion Layer:

Gelatin	1.66 g/m <sup>2</sup>
---------	-----------------------

Magenta dye coupler (various) (see Table II)	0.25-0.38 g/m <sup>2</sup>
---	----------------------------

Coupler solvents (see Table III)	0.10-0.13 g/m <sup>2</sup>
-------------------------------------	----------------------------

Dye stabilizers *	0.76-0.87 g/m <sup>2</sup> total
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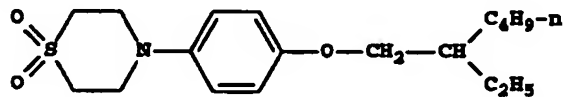
Green-light sensitized silver chloride	0.17 g/m <sup>2</sup>
--	-----------------------

## Subbing Layer:

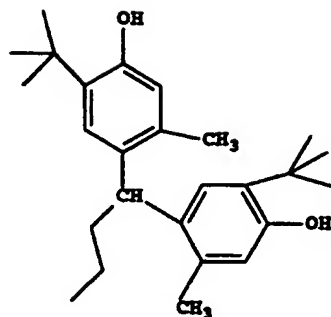
Gelatin	3.24 g/m <sup>2</sup>
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## Resin-coated paper support

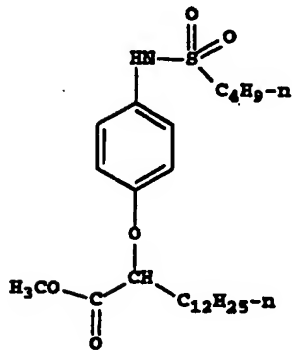
\*Stabilizers were as follows (see Table III for amounts):



ST-3



ST-2



ST-4

Photographic Element II:

## Topcoat:

Gelatin	0.806 g/m <sup>2</sup>
DC-200 (Dow Corning)	0.021 g/m <sup>2</sup>

## UV Absorbing Layer:

Gelatin	0.512 g/m <sup>2</sup>
UV-1	0.130 g/m <sup>2</sup>
UV-2	0.023 g/m <sup>2</sup>
SC-1	0.039 g/m <sup>2</sup>
Dibutyl phthalate	0.026 g/m <sup>2</sup>
1,4-Cyclohexyldimethylene bis(2-ethylhexanoate)	0.026 g/m <sup>2</sup>

## Red-Light Sensitive Layer:

Gelatin	1.39 g/m <sup>2</sup>
Red-light sensitized silver chloride	0.195 g/m <sup>2</sup>
C-1	0.422 g/m <sup>2</sup>
Dibutyl phthalate	0.410 g/m <sup>2</sup>
UV-2	0.272 g/m <sup>2</sup>
SC-1	0.003 g/m <sup>2</sup>
2-(2-Butoxyethoxy)ethyl acetate	0.035 g/m <sup>2</sup>

## Interlayer:

Gelatin	0.735 g/m <sup>2</sup>
UV-1	0.187 g/m <sup>2</sup>
UV-2	0.033 g/m <sup>2</sup>
SC-1	0.055 g/m <sup>2</sup>
Dibutyl phthalate	0.037 g/m <sup>2</sup>
1,4-Cyclohexyldimethylene bis(2-ethylhexanoate)	0.037 g/m <sup>2</sup>

## Green-Light Sensitive Layer:

Gelatin	1.258 g/m <sup>2</sup>
Green-light sensitized silver chloride	See Table IV g/m <sup>2</sup>
M-66	See Table IV g/m <sup>2</sup>
M-29	See Table IV g/m <sup>2</sup>
M-39	See Table IV g/m <sup>2</sup>
Dibutyl phthalate (S-1)	See Table IV g/m <sup>2</sup>
<i>p</i> -Dodecylphenol (S-1a)	See Table IV g/m <sup>2</sup>
2,4-Di- <i>t</i> -amylphenol (S-1b)	See Table IV g/m <sup>2</sup>
Diundecyl phthalate (S-2)	See Table IV g/m <sup>2</sup>
ST-2	See Table IV g/m <sup>2</sup>
ST-3	See Table IV g/m <sup>2</sup>
ST-4	See Table IV g/m <sup>2</sup>

1-Phenyl-5-mercaptopotetrazole 0.001 g/m<sup>2</sup>

## Interlayer:

Gelatin 0.752 g/m<sup>2</sup>

SC-1 0.066 g/m<sup>2</sup>

Dibutyl phthalate 0.187 g/m<sup>2</sup>

## Blue-Light Sensitive Layer:

Gelatin 1.526 g/m<sup>2</sup>

Blue-Light sensitized silver chloride 0.258 g/m<sup>2</sup>

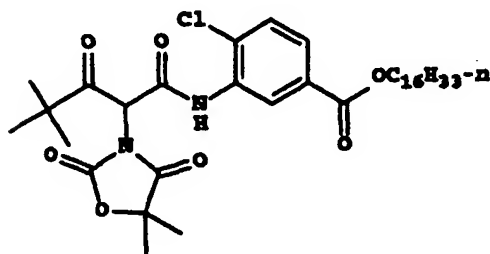
Y-1 0.484 g/m<sup>2</sup>

ST-1 0.484 g/m<sup>2</sup>

Dibutyl phthalate 0.217 g/m<sup>2</sup>

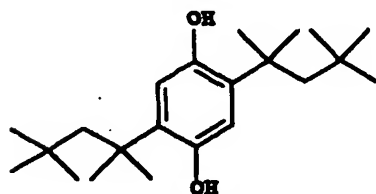
## Resin-coated Paper support

Y-1

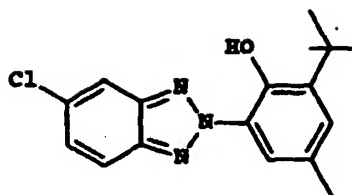


ST-1=N-tert-butylacrylamide / n-butyl acrylate copolymer (50:50)

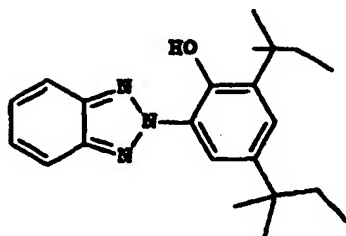
SC-1



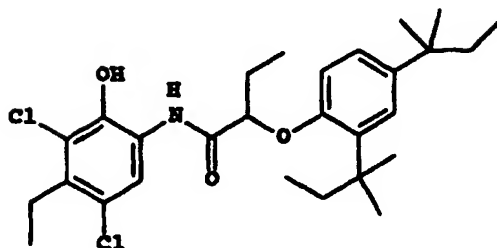
UV-1



UV-2



C-1

**Example 1:**

Samples of Photographic Element I were imagewise exposed and photographically processed using the following processing protocol:

Color development 45 seconds  
 Bleach-fixing 45 seconds  
 Washing (water) 90 seconds.

Color development was carried out using the color developer compositions ("Invention" or "Control") described above. The bleach-fixing composition had the following formulation:

Solution of ammonium thiosulfate (54.4%) & ammonium sulfate (4%)	127.40 g
Sodium metabisulfite	10.00 g
Acetic acid (glacial)	10.20 g
Solution of ammonium ferric	110.40 g

(continued)

ethylenediaminetetraacetate (44%) & ethylenediaminetetraacetic acid (3.5%)	
--	--

Water to make 1 liter of solution pH adjusted to 6.2 at 25 °C
--

The color film samples were thusly processed and suitable color print images were obtained. The magenta dye density in the resulting images was evaluated as noted below. The results are tabulated in Table II below. The loss in magenta dye density is that exhibited when the "Control" developer composition was used compared to when the invention was practiced.

All densities for both Examples 1 and 2 were calculated from densitometry measurements made using a standard densitometer and status-A filters. Data for each color record were measured from a color separation exposed sample exposed by blue, green or red light through a 21-step filter which modulated the light exposure in increments of 0.15 log Exposure.

"Dmax" is the numerical average of all steps up to but not including the first occurrence of three successive steps that are monotonically decreasing in density.

"0.6SH" is the upper scale density point (Shoulder) on the Density vs. Log Exposure curve that corresponds to an exposure that is 0.6 Log Exposure greater than the exposure which gives a density of 0.8.

"0.4SH" is the upper scale density point (Shoulder) on the Density vs. Log Exposure curve that corresponds to an exposure that is 0.4 Log Exposure greater than the exposure which gives a density of 0.8.

"Gamma" is the maximum value of the first derivative of the Density vs. Log Exposure curve.

TABLE II

Magenta Coupler	Amount (g/m <sup>2</sup> )	Developer	Dye Dmax	%Dmax Loss	0.6SH	% Loss	0.4SH	% Loss	Gamma	% Loss
M-29	0.381	Invention	2.527	---	2.298	---	1.925	---	2.918	---
M-29	0.381	Control	2.256	10.7	2.047	10.9	1.785	7.3	2.613	10.5
M-63	0.381	Invention	2.701	---	2.357	---	1.971	---	3.081	---
M-63	0.381	Control	2.412	10.7	2.142	9.1	1.815	7.9	2.702	12.3
M-39	0.296	Invention	2.618	---	2.326	---	1.965	---	3.065	---
M-39	0.296	Control	2.398	8.4	2.136	8.2	1.831	6.8	2.737	10.7
M-37	0.279	Invention	2.521	---	2.271	---	1.938	---	2.982	---
M-37	0.279	Control	2.334	7.4	2.104	7.4	1.833	5.4	2.716	8.9
M-66	0.317	Invention	2.716	---	2.424	---	2.056	---	3.351	---
M-66	0.317	Control	2.572	5.3	2.312	4.6	1.974	3.7	3.149	6.0
M-64	0.254	Invention	2.721	---	2.558	---	2.194	---	3.797	---
M-64	0.254	Control	2.603	4.3	2.416	5.6	2.087	4.9	3.515	7.4
M-64	0.330	Invention	2.951	---	2.821	---	2.377	---	4.342	---
M-64	0.330	Control	2.871	2.7	2.666	5.6	2.243	5.6	3.881	10.6



Table III

Magenta Coupler	Dibutyl Phthalate	Diundecyl Phthalate	ST-3	ST-2	ST-4
M-29	0	0.095	0.190	0.032	0.571
M-63	0	0.102	0.159	0.032	0.565
M-39	0	0.127	0.212	0	0.634
M-37	0.105	0.018	0.232	0	0.634
M-66	0.089	0.038	0.190	0.022	0.613
M-64	0	0.127	0.190	0	0.698
M-64	0	0.127	0.127	0	0.685

It can be seen from the data provided in TABLE II that when the photographic element samples containing the noted magenta dye forming couplers are color developed using the Control developer composition, a loss in dye density is observed. Replacing the antioxidant in the color developer composition with a branched hydroxylamine described herein restored the dye density. Moreover, the low scale portions of the densitometry curves, for example the  $D_{min}$  speed point and toe portions, were unaffected by the use of the hydroxylamine derivatives described herein.

#### Example 2:

Samples of Photographic Element II were imagewise exposed and processed as described above. TABLE IV shows the various amounts of certain components of the green-light sensitive layers in the samples. The cyan, yellow and magenta dye densities were evaluated after processing using either the "Invention" or "Control" color developer compositions as identified above. The results are shown in TABLE V below.

Table IV

Element Sample	Emulsion Coverage	M-66	M-29	M-39	S-1	S-1a	S-1b	S-2	ST-2	ST-3	ST-4
1	0.086	0.249	0	0	0.088	0	0	0.038	0.067	0.190	0.633
2	0.158	0	0.288	0	0	0	0	0.161	0.032	0.212	0.577
3	0.123	0	0	0.254	0	0.254	0	0.101	0	0.153	0.507
4	0.123	0	0	0.254	0	0	0.254	0.101	0	0.153	0.507

Table V

Sample	Developer	Cyan Dmax	Cyan 0.6SH	Cyan 0.4SH	Cyan gamma	Magenta Dmax	Magenta 0.6SH	Magenta 0.4SH	Magenta gamma	Yellow Dmax	Yellow 0.6SH	Yellow 0.4SH	Yellow gamma
1	Control	2.595	2.297	1.950	3.270	2.205	2.099	1.875	3.102	2.335	2.202	1.952	3.336
	Invention	2.732	2.445	2.069	3.484	2.326	2.198	1.940	3.225	2.413	2.323	2.088	3.779
3	Control	2.600	2.302	1.965	3.174	2.235	2.111	1.874	3.115	2.330	2.206	1.958	3.346
	Invention	2.711	2.442	2.078	3.505	2.462	2.331	2.036	3.519	2.394	2.313	2.075	3.701
4	Control	2.633	2.329	1.982	3.236	2.177	2.049	1.817	2.901	2.336	2.212	1.957	3.342
	Invention	2.737	2.475	2.094	3.565	2.436	2.295	2.010	3.488	2.390	2.299	2.068	3.677
2	Control	2.601	2.295	1.963	3.177	2.210	2.067	1.841	3.026	2.376	2.237	1.988	3.478
	Invention	2.726	2.421	2.062	3.455	2.410	2.283	1.998	3.400	2.430	2.347	2.100	3.757

The data in Table V show that when the Control developer was used to process the noted samples, a loss in magenta dye density was observed. Replacing the antioxidant with the branched hydroxylamine in the "Invention" Developer restored the magenta dye density. The yellow and cyan dye densities were generally less sensitive to the

color developer used in processing. Moreover, the low scale portions of the densitometry curves, for example the  $D_{\min}$  speed point and toe portions, were unaffected by the use of the hydroxylamine derivatives described herein.

# Claims

## 1. A method of processing comprising:

color developing an imagewise exposed color photographic silver halide material with a color developer composition comprising:

- (a) a color developing agent present in an amount of at least 0.001 mol/l, and
- (b) a hydroxylamine derivative characterized as having the formula I:



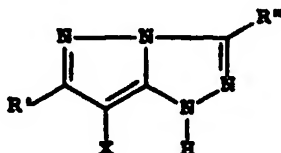
wherein R and  $\text{R}^1$  are independently alkyl groups of 1 to 8 carbon atoms provided the total carbon atoms for R and  $\text{R}^1$  is no greater than 9,

$\text{R}^2$  is an alkylene group of 2 to 6 carbon atoms, or a phenylene or benzylene group, and

Y is sulfo, carboxy, hydroxy, phosphono,  $-\text{SO}_2\text{NR}^3\text{R}^4$  or  $-\text{CONR}^3\text{R}^4$  wherein  $\text{R}^3$  and  $\text{R}^4$  are independently hydrogen or an alkyl group of 1 to 3 carbon atoms,

the hydroxylamine derivative being present in the color developer composition in an amount of at least 0.001 mol/l,

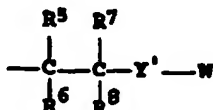
wherein the photographic material comprises at least one silver halide emulsion layer, the layer having in reactive association therewith, at least one magenta dye-forming coupler represented by the formula II:



wherein

X is hydrogen or a coupling-off group,

$\text{R}'$  is a tertiary alkyl group,  $\text{R}''$  represents the group



$\text{R}^5$ ,  $\text{R}^6$ , and  $\text{R}^7$  are independently hydrogen or alkyl groups, and any two of  $\text{R}^5$ ,  $\text{R}^6$ , and  $\text{R}^7$  can together form a ring,

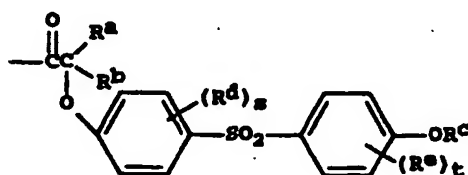
$\text{R}^8$  is hydrogen or a substituent, provided that  $\text{R}^7$  and  $\text{R}^8$  can together form a ring when  $\text{R}^8$  is a substituent,

$\text{Y}'$  is  $-\text{NH}-$  or  $-\text{CH}_2-$ , and

W is selected from the group consisting of  $-\text{C}(\text{O})\text{R}^9$ ,  $-\text{SO}_2\text{R}^9$  and  $-\text{P}(\text{O})(\text{OR}^{10})_2$  wherein  $\text{R}^9$  is any of an alkyl, aryl, alkoxy, aryloxy, alkylamino or arylamino group, and  $\text{R}^{10}$  is an alkyl or aryl group.

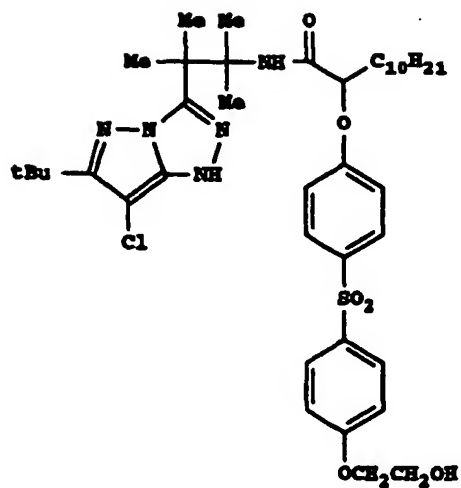
- 2. The method as claimed in claim 1 wherein R and  $\text{R}^1$  are independently an alkyl group of 1 to 3 carbon atoms,  $\text{R}^2$  is an unsubstituted phenylene group, unsubstituted benzylene group or an unsubstituted alkylene group of 2 to 4 carbon atoms, Y is sulfo, carboxy,  $-\text{SO}_2\text{NR}^3\text{R}^4$  or  $-\text{CONR}^3\text{R}^4$ , wherein  $\text{R}^3$  and  $\text{R}^4$  are independently hydrogen, methyl group or ethyl group.

3. The method as claimed in either claim 1 or 2 wherein R and R<sup>1</sup> are independently a methyl or ethyl group, and Y is sulfo or carboxy.
4. The method as claimed in any of claims 1 to 3 wherein the hydroxylamine is N-isopropyl-N-(2-ethylenesulfonic acid)hydroxylamine, N-sec-butyl-N-(2-ethylenesulfonic acid)hydroxylamine, N-isopropyl-N-(1-methylpropionic acid)hydroxylamine, N-isopropyl-N-(3-carboxypropyl)hydroxylamine, N-sec-butyl-N-(2-carboxyethyl)hydroxylamine, N-sec-butyl-N-(1-methyl-2-carboxyethyl)hydroxylamine, N-sec-butyl-N-(4-carboxybutyl)hydroxylamine, N-octyl-N-(3-carboxypropyl)hydroxylamine, N-isopropyl-N-(2-ethanephosphonic acid)hydroxylamine, N-isopropyl-N-(2-sulfonamidoethyl)hydroxylamine, N-isopropyl-N-(2-N-isopropylsulfonamidoethyl)hydroxylamine, N-isopropyl-N-(*p*-carboxybenzyl)hydroxylamine, N-isopropyl-N-(2-carboxyethyl)hydroxylamine, N-isopropyl-N-(2-N',N'-dimethylsulfonamidoethyl)-hydroxylamine, N-isopropyl-N-(2-N',N'-diethylsulfonamidoethyl)hydroxylamine, N-isopropyl-N-(2,2-dicarboxyethyl)hydroxylamine, N-sec-butyl-N-(2-carboxyethyl)hydroxylamine, N-isopropyl-N-(2-carbonamidoethyl)hydroxylamine, N-isopropyl-N-(2-N',N'-dimethylcarbonamidoethyl)hydroxylamine, N-isopropyl-N-(2-N'-isopropylcarbonamidoethyl)-hydroxylamine, or a salt or ester of a free acid in this list.
5. The method as claimed in any of claims 1 to 4 wherein color photographic material is a photographic color paper having a reflective support
6. The method of claims 1 to 5 wherein the color photographic material has at least one high silver chloride emulsion containing the dye-forming coupler, and the silver coverage in the color photographic material is less than 0.8 g Ag/m<sup>2</sup>.
7. The method as claimed in any of claims 1 to 6 wherein R<sup>1</sup> is a *t*-butyl, 1-methyl-1-cyclopropyl, *t*-pentyl, *t*-octyl or adamantyl group, and X is hydrogen, halo or an aryloxy group.
8. The method as claimed in any of claims 1 to 7 wherein R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently an alkyl group of 1 to 6 carbon atoms, or any two of them together can form a cycloalkyl group having 5 or 6 carbon atoms in the ring, and R<sup>8</sup> is hydrogen, methyl group or ethyl group, or together, R<sup>7</sup> and R<sup>8</sup> form a cycloalkyl group having 5 or 6 carbon atoms in the ring.
9. The method as claimed in any of claims 1 to 8 wherein W is -C(O)R<sup>9</sup> or -SO<sub>2</sub>R<sup>9</sup> wherein R<sup>9</sup> is an alkyl group.
10. The method of claim 9 wherein W is -C(O)R<sup>9</sup> and further contains the group -NHC(O)R<sup>11</sup> wherein R<sup>11</sup> is an alkyl or aryl group.
11. The method of claim 9 wherein W is

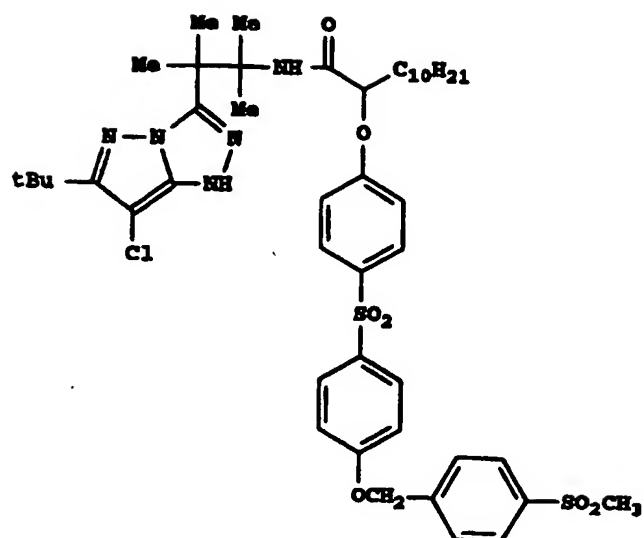


wherein R<sup>a</sup> and R<sup>b</sup> are independently hydrogen, or an alkyl or aryl group, R<sup>c</sup> is a substituent, R<sup>d</sup> and R<sup>e</sup> are independently selected substituents, and s and t are independently integers of from 0 to 4. and R<sup>c</sup> is a phenylmethylenesulfonyl group.

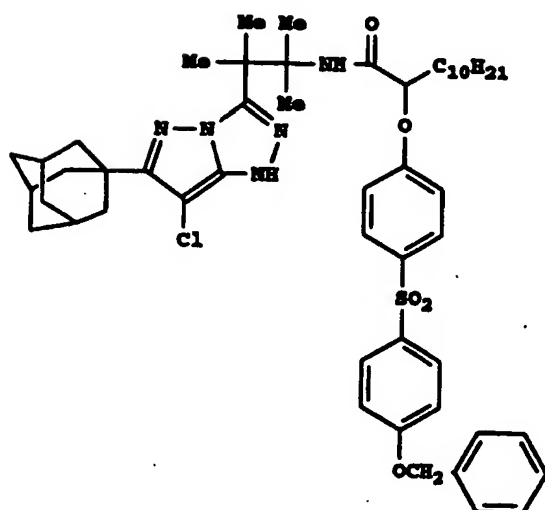
12. The method as claimed in any of claims 1 to 11 wherein the magenta dye-forming coupler is selected from the group consisting of:



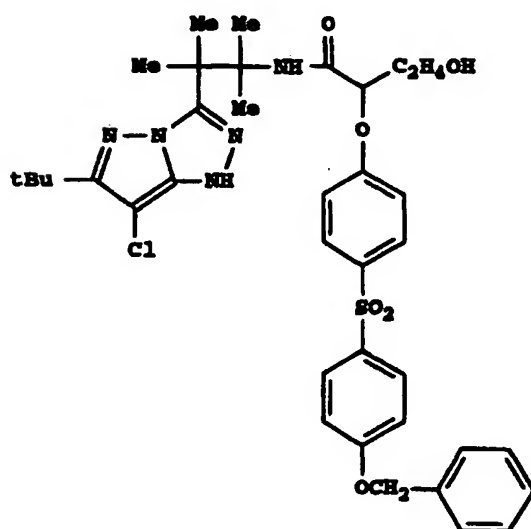
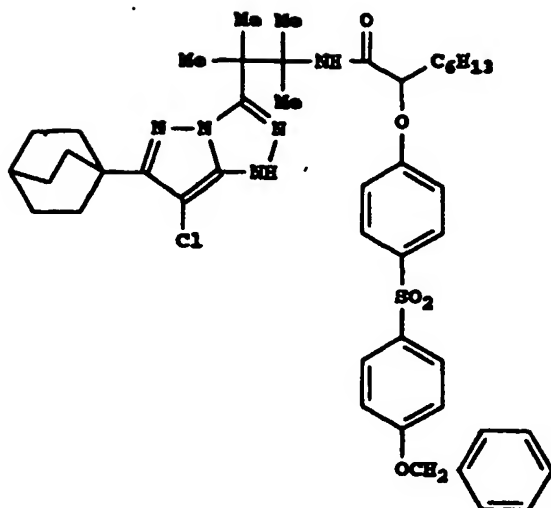
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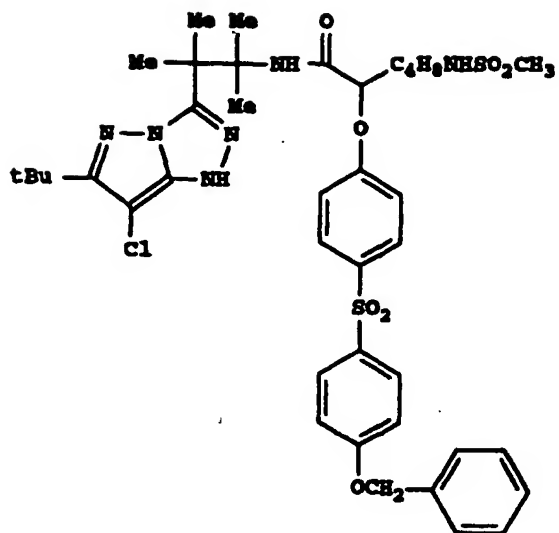


M-2

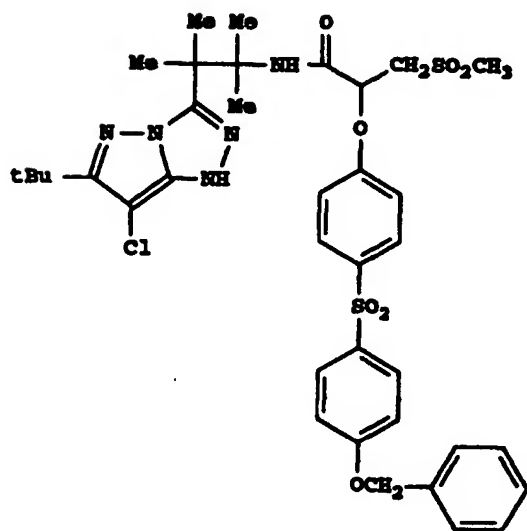


M-3



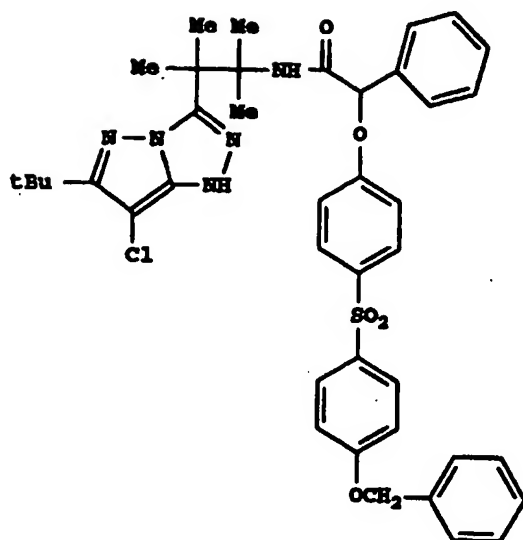


M-6

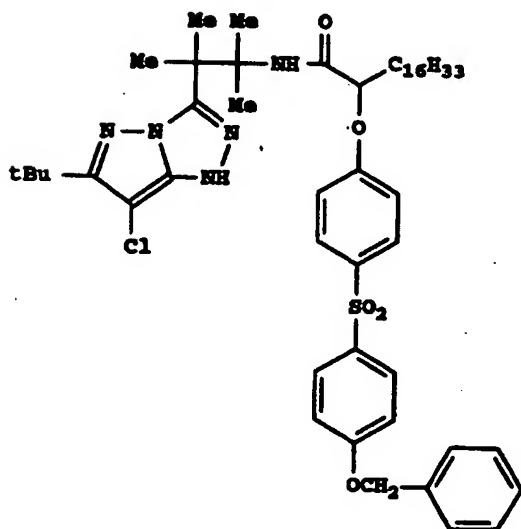


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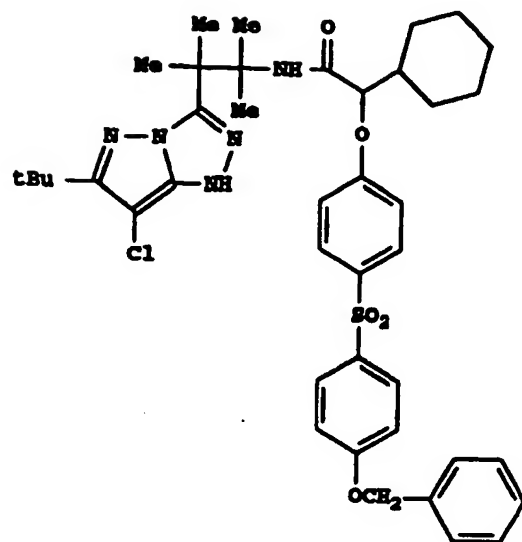




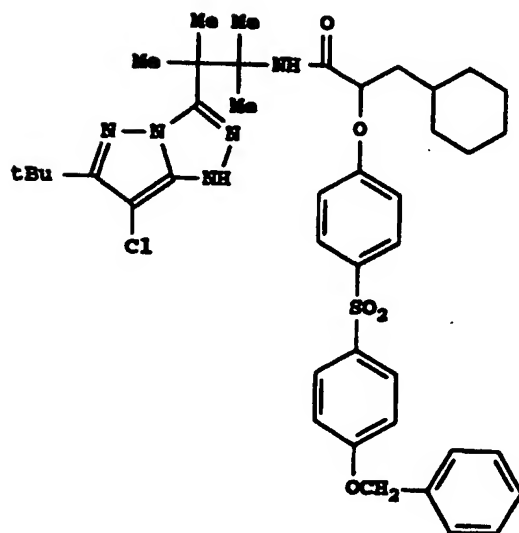
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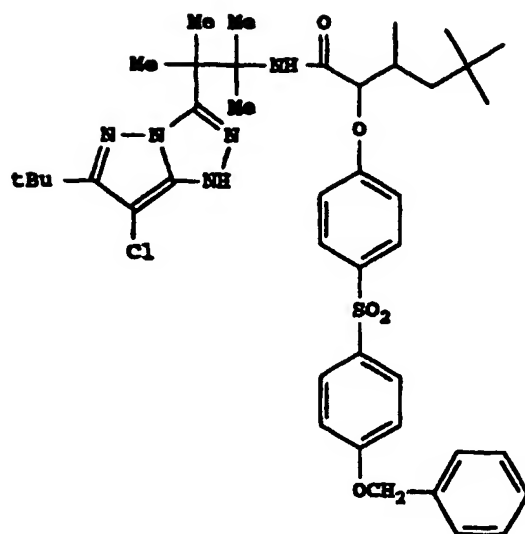
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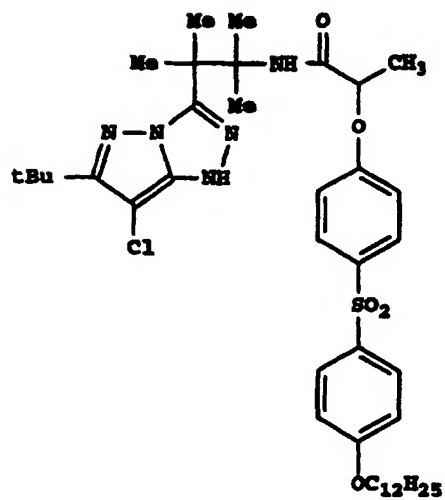
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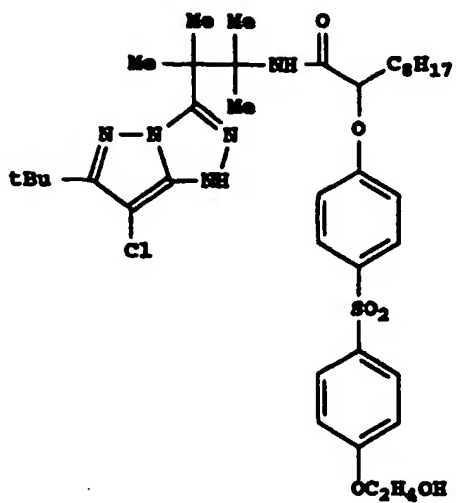
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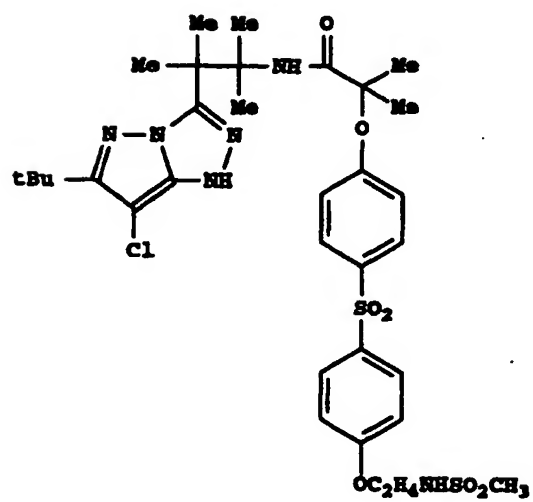
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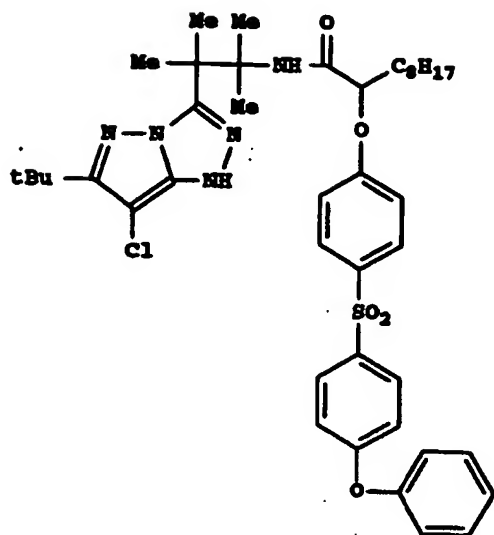
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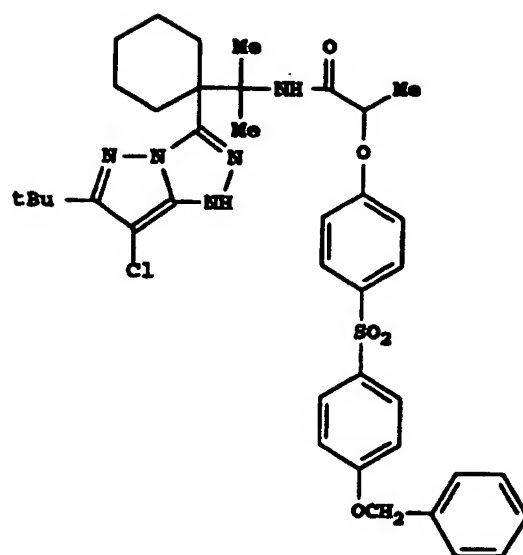
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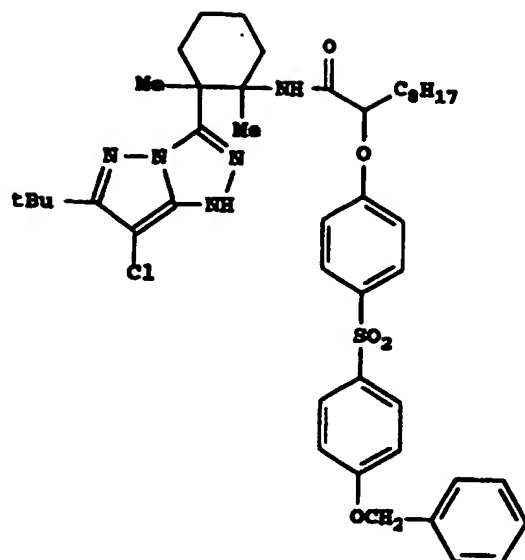
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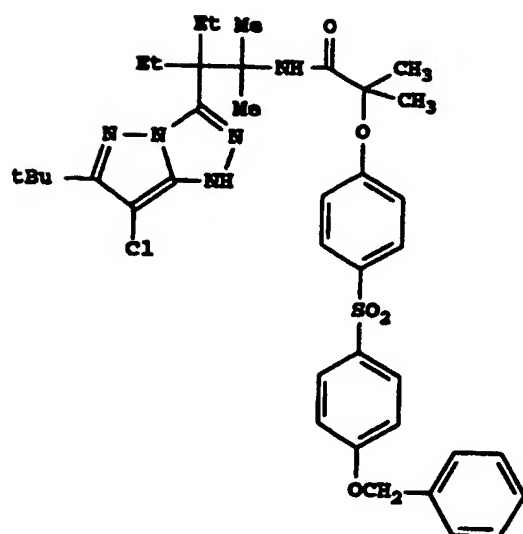
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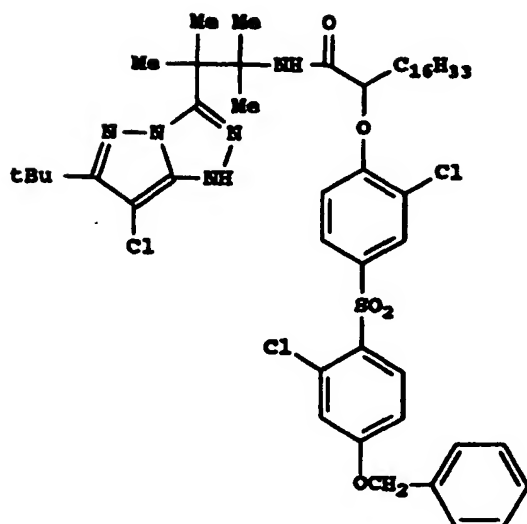
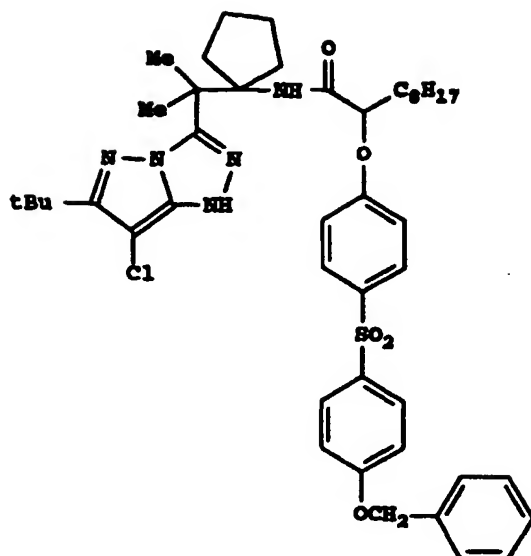
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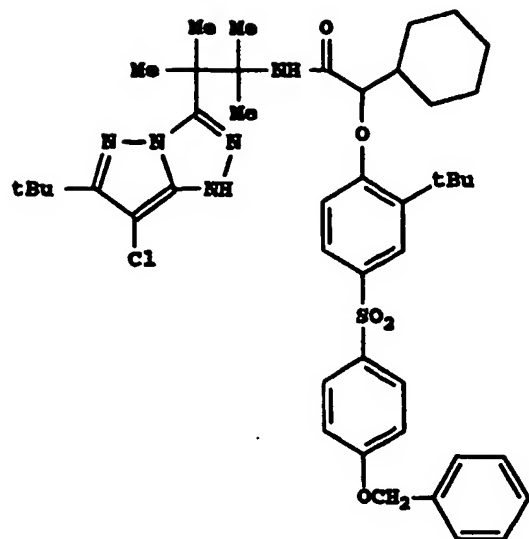


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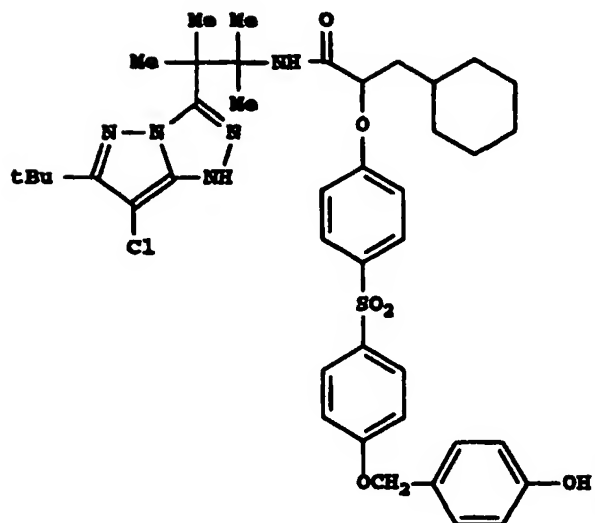


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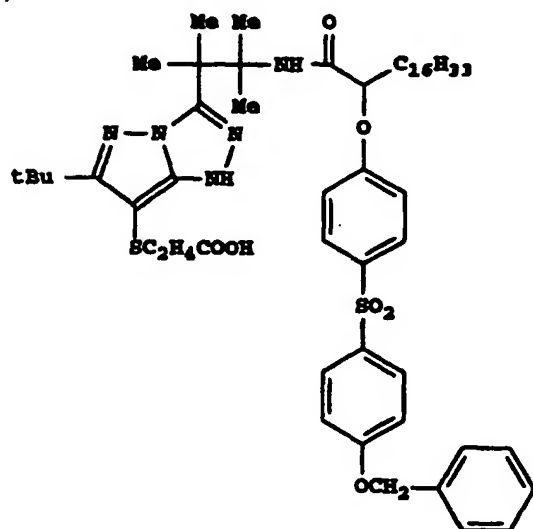
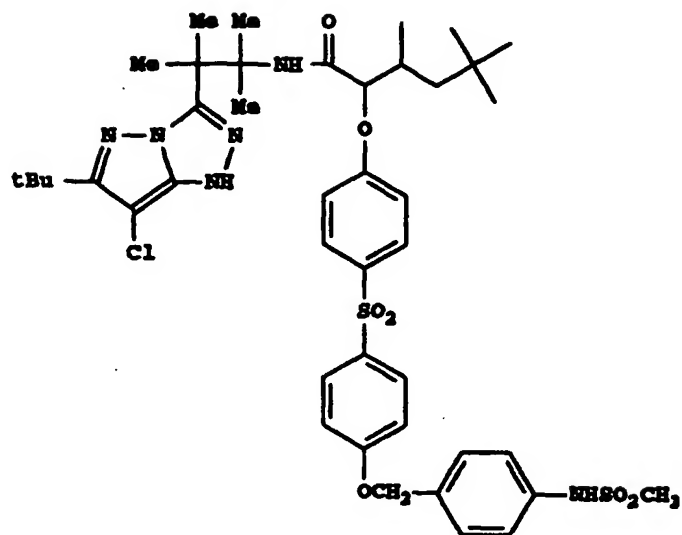


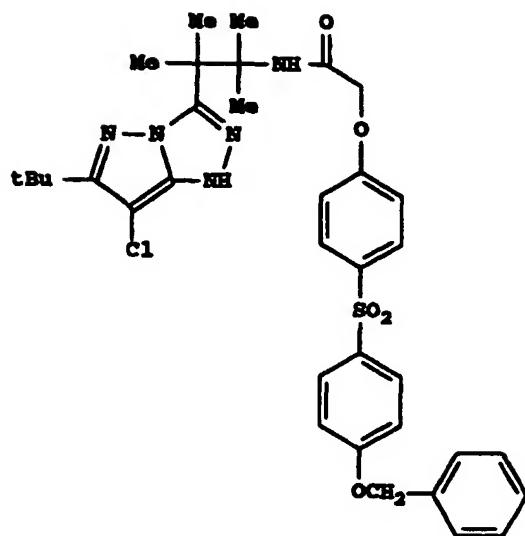
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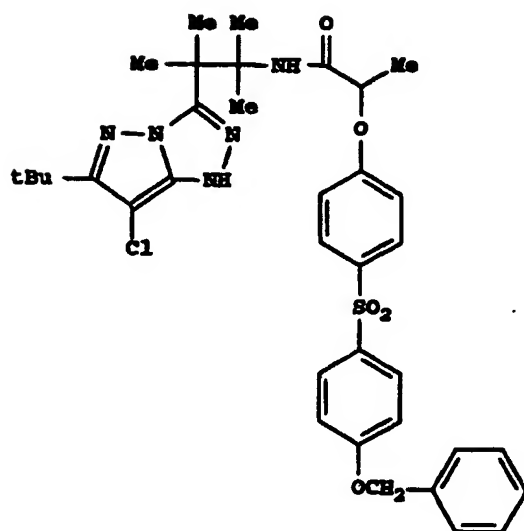
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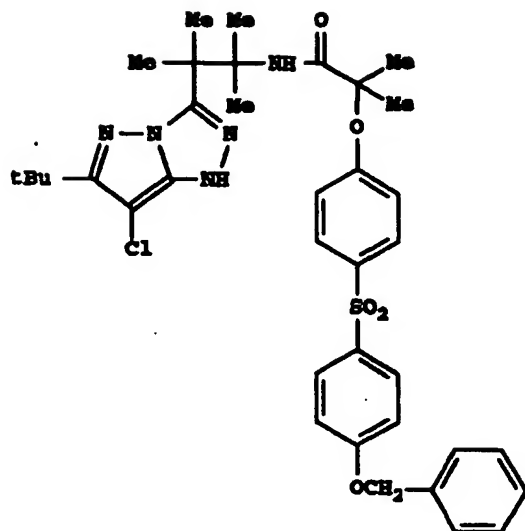




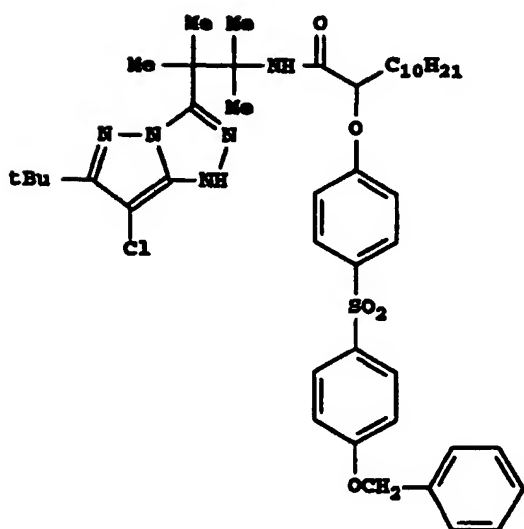
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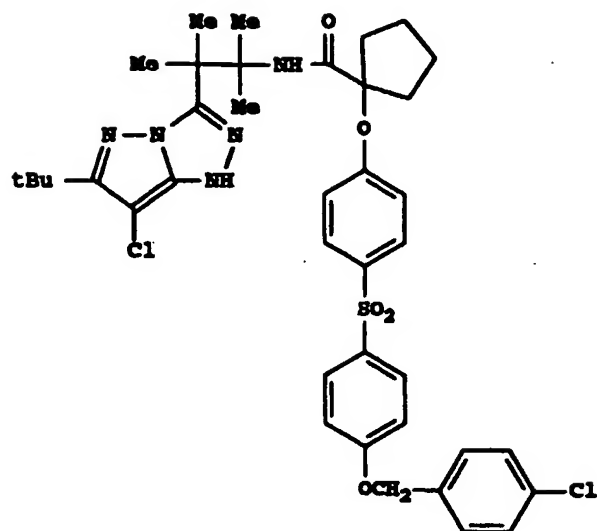
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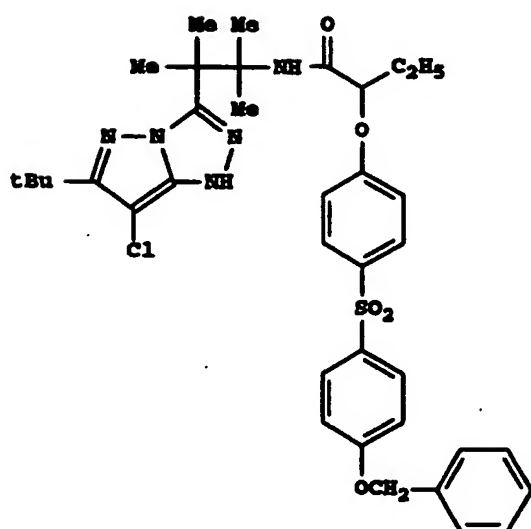
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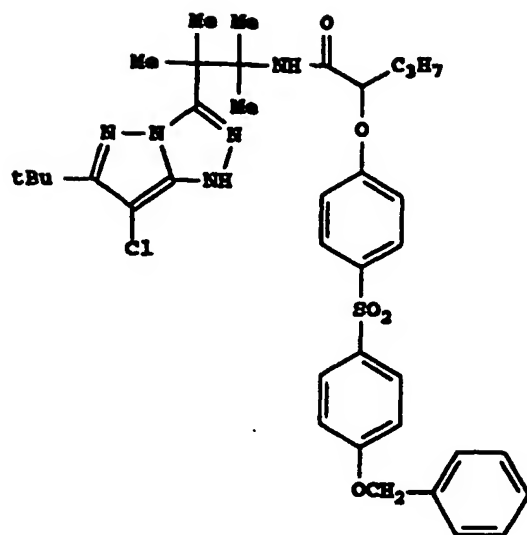
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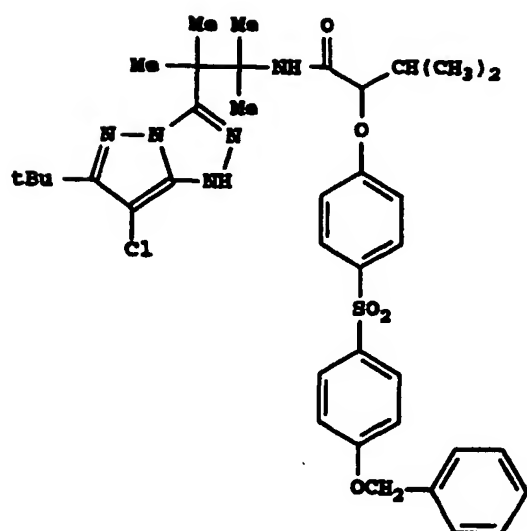
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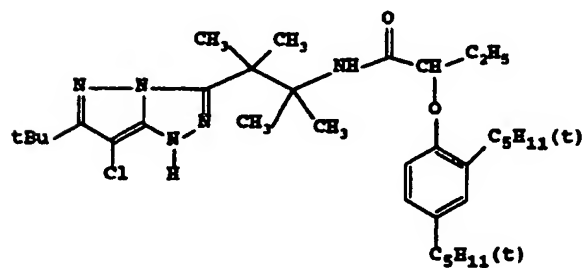
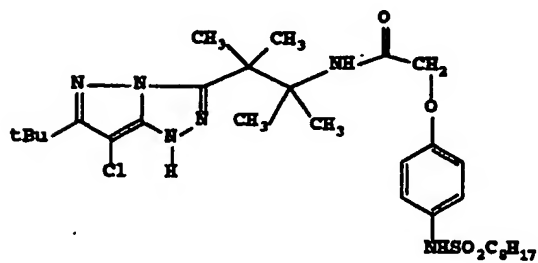
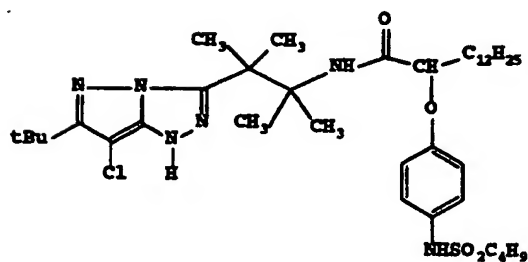
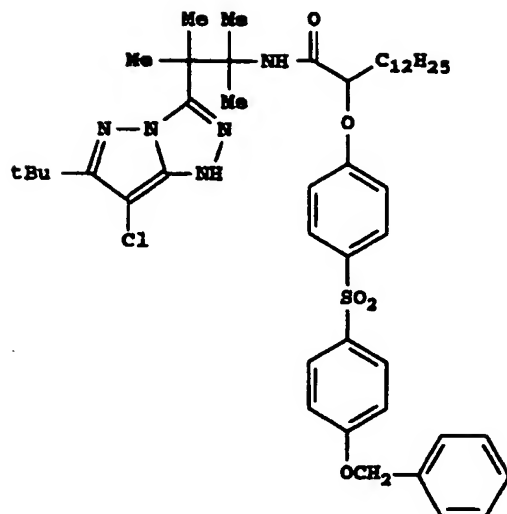
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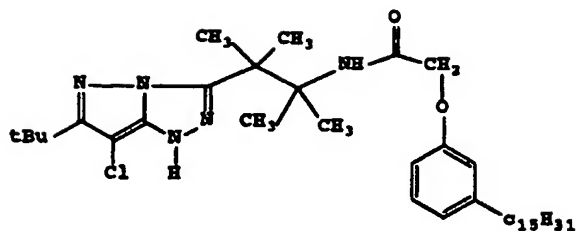


M-34

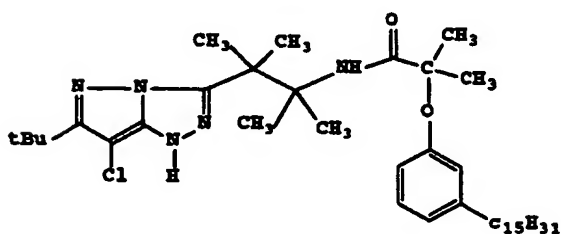


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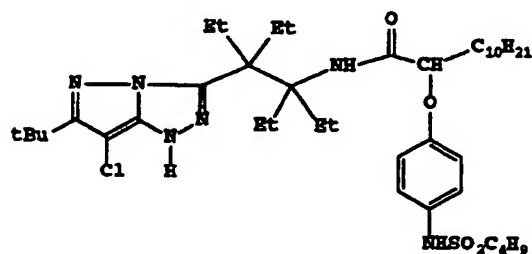




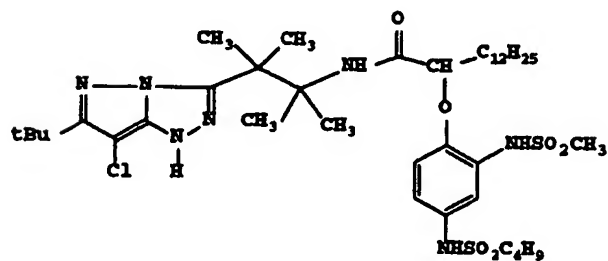
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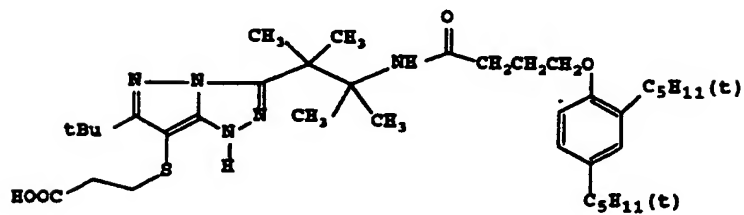
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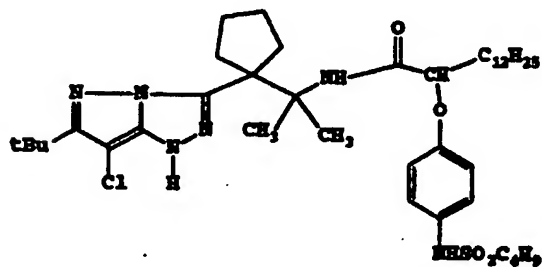
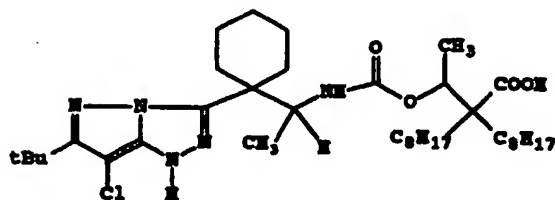
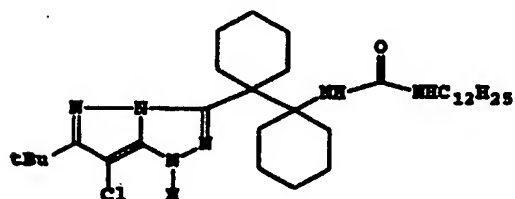
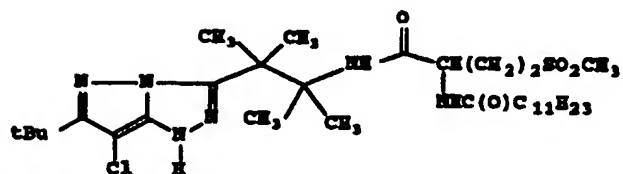
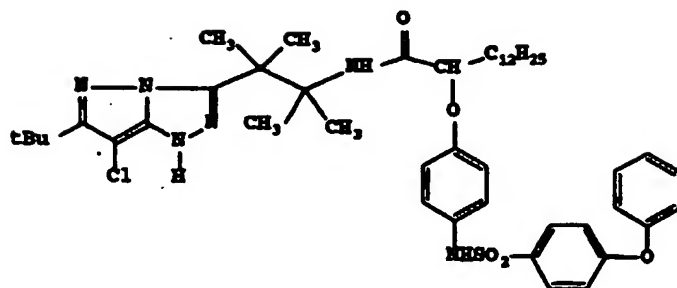
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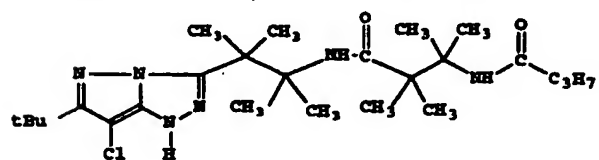
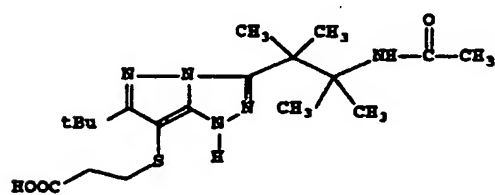
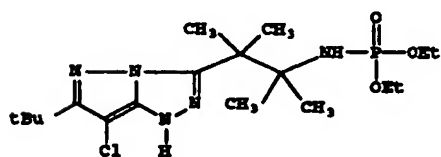
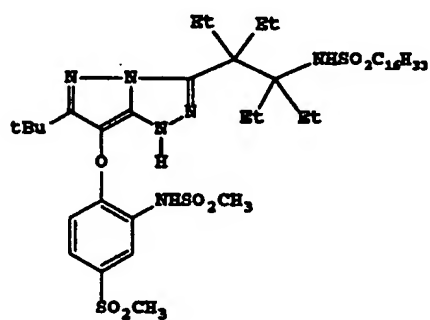
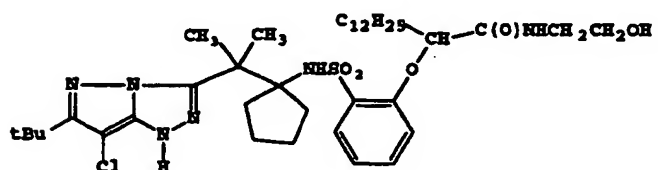
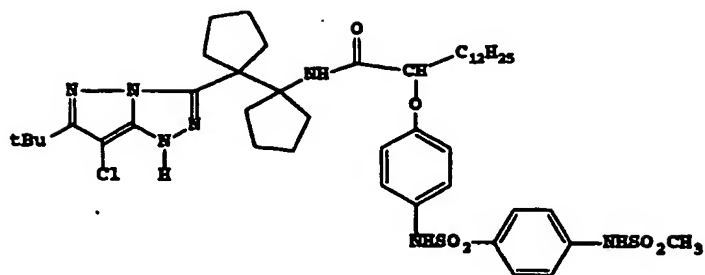
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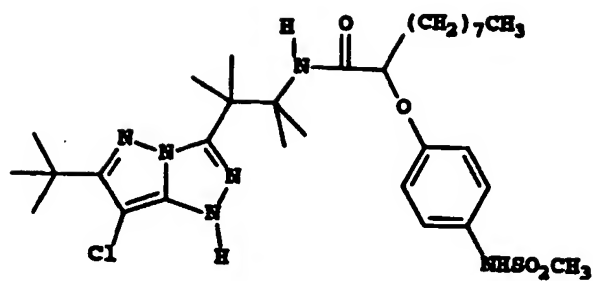


M-44

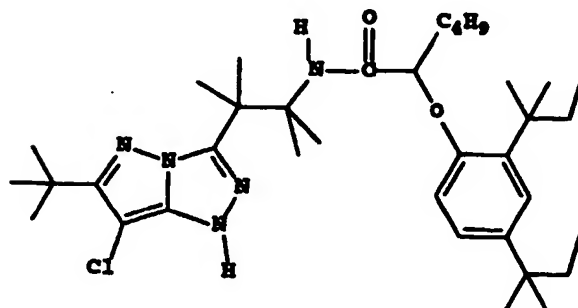




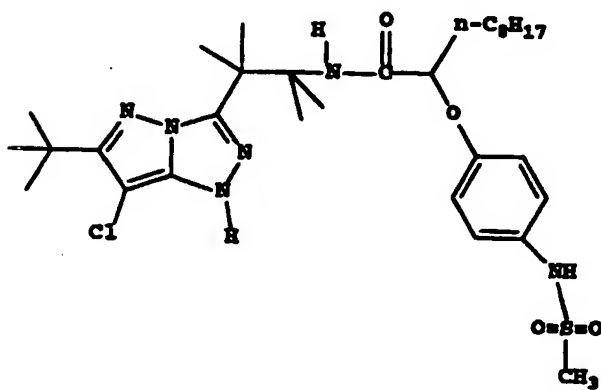




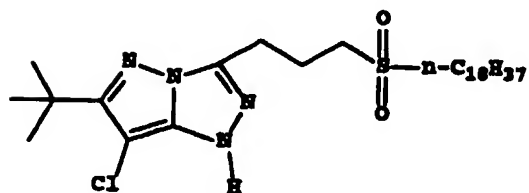
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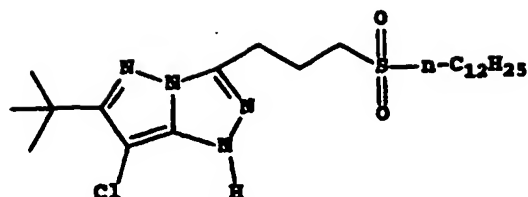
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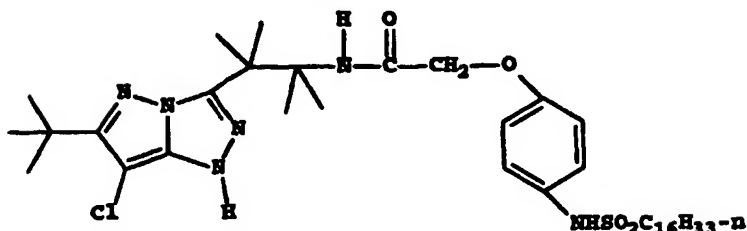
M-64



M-65

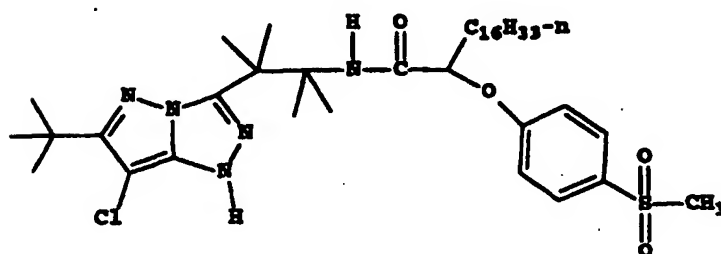


M-66



M-67

and



M-68

13. The method as claimed in any of claims 1 to 12 wherein the magenta dye-forming coupler is present in a silver halide emulsion layer that is sensitive to green light and that contains silver at a coverage of less than 0.25 g/m<sup>2</sup>.
14. The method as claimed in any of claims 1 to 13 wherein the magenta dye-forming coupler is present in admixture with a coupler solvent that is diundecyl phthalate, dibutyl phthalate or oleyl alcohol, the coupler solvent being present in an amount of at least 0.06 g/m<sup>2</sup>.
15. The method as claimed in claim 13 wherein the green light sensitive emulsion layer comprises silver halide grains comprising at least 90 mol % silver chloride and less than 1 mol % silver iodide.
16. The method as claimed in any of claims 1 to 15 wherein the color developing is carried out for less than 60 seconds.
17. The method as claimed in claim 16 wherein the photographic silver halide material is a color photographic paper, and the method further comprises a bleach-fixing step and a washing step, and the time for the entire method is less than 90 seconds.
18. The method as claimed in claim 17 wherein the time for the color developing is from 5 to 30 seconds.
19. The method as claimed in any of claims 1 to 18 wherein the magenta dye-forming coupler is the compound identified as M-29.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 98 20 1823

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	WO 96 28761 A (KODAK) 19 September 1996 * page 3, line 18 - page 7, line 3 * * page 7, line 25 - line 28 * * page 10, line 10 - line 19 * * page 11, line 23 - line 27 * * page 12, line 22 - line 31 * * page 17; table I *	1-18	G03C7/413 G03C7/38
Y	US 5 013 633 A (YOSHIZAWA ET AL.) 7 May 1991 * column 15; example M34 * * column 27, line 3 - line 6 * * column 43, line 66 - column 44, line 2 * * column 44, line 55 - line 61 * * column 47, line 61 - line 65 * * column 48, line 12 - line 14 * * column 56; table 1 * * column 56, line 64 - line 68 *	1-18	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>28 August 1998</b>	Examiner <b>Magrinos, S</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/92 (P4/C01)